



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : H01J 1/63, H05B 33/14		A1	(11) International Publication Number: WO 98/28767 (43) International Publication Date: 2 July 1998 (02.07.98)																																	
(21) International Application Number: PCT/US97/23952 (22) International Filing Date: 23 December 1997 (23.12.97) (30) Priority Data: <table border="0"> <tr><td>08/774,119</td><td>23 December 1996 (23.12.96)</td><td>US</td></tr> <tr><td>08/774,120</td><td>23 December 1996 (23.12.96)</td><td>US</td></tr> <tr><td>08/772,332</td><td>23 December 1996 (23.12.96)</td><td>US</td></tr> <tr><td>08/771,815</td><td>23 December 1996 (23.12.96)</td><td>US</td></tr> <tr><td>08/814,976</td><td>11 March 1997 (11.03.97)</td><td>US</td></tr> <tr><td>08/821,380</td><td>20 March 1997 (20.03.97)</td><td>US</td></tr> <tr><td>08/838,099</td><td>15 April 1997 (15.04.97)</td><td>US</td></tr> <tr><td>08/850,264</td><td>2 May 1997 (02.05.97)</td><td>US</td></tr> <tr><td>08/865,491</td><td>29 May 1997 (29.05.97)</td><td>US</td></tr> <tr><td>08/925,403</td><td>9 September 1997 (09.09.97)</td><td>US</td></tr> <tr><td>08/928,800</td><td>12 September 1997 (12.09.97)</td><td>US</td></tr> </table> (71) Applicants: THE TRUSTEES OF PRINCETON UNIVERSITY [US/US]; P.O. Box 36, Princeton, NJ 08544 (US). THE UNIVERSITY OF SOUTHERN CALIFORNIA [US/US]; The University of Southern California Park, Los Angeles, CA 90089 (US).		08/774,119	23 December 1996 (23.12.96)	US	08/774,120	23 December 1996 (23.12.96)	US	08/772,332	23 December 1996 (23.12.96)	US	08/771,815	23 December 1996 (23.12.96)	US	08/814,976	11 March 1997 (11.03.97)	US	08/821,380	20 March 1997 (20.03.97)	US	08/838,099	15 April 1997 (15.04.97)	US	08/850,264	2 May 1997 (02.05.97)	US	08/865,491	29 May 1997 (29.05.97)	US	08/925,403	9 September 1997 (09.09.97)	US	08/928,800	12 September 1997 (12.09.97)	US	(72) Inventors: THOMPSON, Mark, E.; 4447 Pepper Creek Way, Anaheim Hills, CA 92807 (US). FORREST, Stephen, R.; 148 Hunt Drive, Princeton, NJ 08540 (US). BURROWS, Paul; 413 Clarksville Road, Princeton Junction, NJ 08550 (US). GARBUZOV, Dmitri, Z.; 5-V Hibben Apartments, Faculty Road, Princeton, NJ 08540 (US). SHEN, Zilan; 20212 Heather Drive, Lawrenceville, NJ 08648 (US). CRONIN, Jon, A.; Apartment 3, 2044 Ambergate Lane, Cordova, TN 38010 (US). YOU, Yujian; 5367 San Vincenti Boulevard No. 232, Los Angeles, CA 90007 (US). SHOUSTIKOV, Andrei; 1175 W 29th Street No. 8, Los Angeles, CA 90007 (US). (74) Agents: MEAGHER, Thomas, F. et al.; Kenyon & Kenyon, One Broadway, New York, NY 10004 (US). (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
08/774,119	23 December 1996 (23.12.96)	US																																		
08/774,120	23 December 1996 (23.12.96)	US																																		
08/772,332	23 December 1996 (23.12.96)	US																																		
08/771,815	23 December 1996 (23.12.96)	US																																		
08/814,976	11 March 1997 (11.03.97)	US																																		
08/821,380	20 March 1997 (20.03.97)	US																																		
08/838,099	15 April 1997 (15.04.97)	US																																		
08/850,264	2 May 1997 (02.05.97)	US																																		
08/865,491	29 May 1997 (29.05.97)	US																																		
08/925,403	9 September 1997 (09.09.97)	US																																		
08/928,800	12 September 1997 (12.09.97)	US																																		
(54) Title: AN ORGANIC LIGHT EMITTING DEVICE CONTAINING A PROTECTION LAYER																																				
(57) Abstract The present invention is directed to organic light emitting devices comprised of a heterostructure for producing electroluminescence, wherein the heterostructure includes a protection layer between a hole transporting layer and an indium tin oxide anode layer. The hole injection enhancement layer may be comprised of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA), bis(1,2,5-thiadiazolo)-p-quinobis(1,3-dithiole) (BTQBT), or other suitable, rigid organic materials. The present invention is further directed to methods of fabricating such devices, wherein the devices may include alternative combinations of materials for each of the layers included in the devices.																																				

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

AN ORGANIC LIGHT EMITTING DEVICE
CONTAINING A PROTECTION LAYER

5

FIELD OF THE INVENTION

The present invention is directed to organic light emitting devices comprised of a protection layer between the hole transporting layer and the ITO anode layer.

10

BACKGROUND OF THE INVENTION

Organic light emitting devices (OLEDs) are light emitting devices that are comprised of several layers, in which one of the layers is comprised of an organic material that can be made to electroluminesce by applying a voltage across the device, *C.W. Tang et al., Appl. Phys. Lett 51, 913 (1987)*. Certain OLEDs have been shown to have sufficient brightness, range of color and operating lifetimes for use as a practical alternative technology to LCD-based full color flat-panel displays (*S.R. Forrest, P.E. Burrows and M.E. Thompson, Laser Focus World, Feb. 1995*). Furthermore, since many of the organic thin films used in such devices are transparent in the visible spectral region, they allow for the realization of a completely new type of display pixel in which the red (R), green (G), and blue (B) emission layers are placed in a vertically stacked geometry to provide a simple fabrication process, a small R-G-B pixel size, and a large fill factor.

A transparent OLED (TOLED) which represents a significant step toward realizing high resolution, independently addressable stacked R-G-B pixels has been reported in International Patent Application Nos. PCT/US95/15790 and PCT/US97/02681. Such TOLEDs are disclosed to be capable of having greater than 71% transparency when turned off and of emitting light from both top and bottom device surfaces with high efficiency (approaching 1% quantum efficiency) when the device is turned on. The TOLED uses transparent indium tin oxide (ITO) as the hole-injecting electrode and a Mg-Ag-ITO layer for electron-injection. A device was disclosed in which the Mg-Ag-ITO electrode was used as a hole-injecting contact for a second,

different color-emitting OLED stacked on top of the TOLED. Each device in the stacked OLED (SOLED), which is comprised of multiple vertically stacked layers, was independently addressable and emitted its own characteristic color through
5 the transparent organic layers, the transparent contacts and the glass substrate, allowing the device to emit any color that could be produced by varying the relative output of the red and blue color-emitting layers.

10 Thus, publication of PCT/US95/15790 provided disclosure of an integrated OLED where both intensity and color could be independently varied and controlled with external power supplies in a color tunable display device. As such, PCT/US95/15790 illustrates a principle for achieving
15 integrated, full color pixels that provide high image resolution, which is made possible by the compact pixel size. Furthermore, relatively low cost fabrication techniques, as compared with prior art methods, may be utilized for making such devices.

20

Devices whose structure is based upon the use of layers of organic optoelectronic materials generally rely on a common mechanism leading to optical emission. Typically, this mechanism is based upon the radiative recombination of a
25 trapped charge. Specifically, organic light emitting devices comprise at least two thin organic layers separating the anode and cathode of the device. The material of one of these layers is specifically chosen based on the material's ability to transport holes (the "hole transporting layer" or "HTL") and
30 the material for one of the other layers is specifically selected according to its ability to transport electrons (the "electron transporting layer" or "ETL"). With such a construction, the device can be viewed as a diode with a forward bias when the potential applied to the anode is higher
35 than the potential applied to the cathode. Under these bias conditions, the anode injects holes (positive charge carriers) into the hole transporting layer, while the cathode injects

electrons into the electron transporting layer. The portion of the luminescent medium adjacent to the anode thus forms a hole injecting and transporting zone while the portion of the luminescent medium adjacent to the cathode forms an electron
5 injecting and transporting zone. The injected holes and electrons each migrate toward the oppositely charged electrode. When an electron and hole localize on the same molecule, a Frenkel exciton is formed. Recombination of this short-lived state may be visualized as an electron dropping
10 from its conduction potential to a valence band, with relaxation occurring, under certain conditions, preferentially via a photoemissive mechanism. Under this view of the mechanism of operation of typical thin-layer organic devices, the electroluminescent layer comprises a luminescence zone
15 receiving mobile charge carriers (electrons and holes) from each electrode.

The materials that produce the electroluminescent emission are frequently the same materials that function either as the
20 electron transporting layer or as the hole transporting layer. Such devices are referred to as having a single heterostructure. Alternatively, the electroluminescent material may be present in a separate emissive layer between the hole transporting layer and the electron transporting
25 layer in what is referred to as a double heterostructure.

In addition to having the emissive material present as the primary material in the electron transporting layer or in the hole transporting layer, the emissive material may also be
30 present as a dopant that is contained within a host material. Materials that are present as host and dopant are selected so as to have efficient energy transfer between the host and dopant materials. It is desirable for OLEDs to be fabricated using materials that provide electroluminescent emission in a
35 relatively narrow band centered near selected spectral regions, which correspond to one of the three primary colors, red, green and blue so that they may be used as a colored

layer in an OLED or SOLED. It would be desirable, in particular, to be able to select these compounds from classes of compounds in which the emission may be varied by selectively varying the substituents or by modifying the structure of the base compound that produces emission. In addition, these materials need to be capable of producing acceptable electrical properties for the OLED. Furthermore, such host and dopant materials are preferably capable of being incorporated into the OLED using starting materials that can be readily incorporated into the hole transporting layer or electron transporting layer using convenient fabrication techniques.

Demonstration of efficient electroluminescence from vacuum deposited molecular organic light emitting devices has generated interest in their potential application for emissive flat panel displays. To be useful in low cost, active matrix displays, device structures which are integratable with pixel electronics need to be demonstrated. A conventional OLED is grown on a transparent anode such as ITO, and the emitted light is viewed through the substrate, complicating integration with electronic components such as silicon-based display drivers. It is therefore desirable to develop an OLED with emission through a top, transparent contact. A surface-emitting polymer-based OLED grown on silicon with a transparent ITO and a semitransparent Au or Al top anode has been demonstrated, *D.R. Baigent, et al., Appl. Phys. Lett.* 65, 2636 (1994); *H.H. Kim, et al., J. Lightwave Technol.* 12, 2107 (1994).

A similar integration of molecular OLEDs with silicon was achieved using a tunneling SiO₂ interface, Kim et al. The tunneling interface, however, increases the device operating voltage, and can be avoided in structures such as for the recently reported transparent TOLEDs, *V. Bulovic, et al., Nature* 380, 29 (1996). *G.Gu, Et al., Appl. Phys. Lett.* 68, 2606 (1996), which can, in principle, be grown on a silicon

substrate. The TOLED anode, however, forms the electrode contact which is in direct contact with the substrate, "the bottom contact", whereas for display drivers employing n-channel field effect transistors (NFETs), such as amorphous silicon NFETs, it would be desirable for the bottom contact of the OLED to be the cathode. This would require fabricating inverted OLEDs (IOLEDs), that is, devices in which the order of placing the sequence of layers onto the substrate is reversed. For example, for a single heterostructure OLED, the electron-injecting cathode layer is deposited onto the substrate, the electron transporting layer is deposited on the cathode, the hole transporting layer is deposited on the electron transporting layer and the hole-injecting anode layer is deposited on the hole transporting layer.

Fabrication of such IOLEDs, thus requires that the ITO anode layer be sputter-deposited directly or indirectly onto relatively fragile organic thin films. Since the ITO layer is typically deposited using conventional sputtering or electron beam methods so as to produce layers having a thickness from about 500 Å up to as much as 4000 Å, it is desirable that these layers be deposited at the highest deposition rates possible so as to reduce the time necessary to prepare such layers. For example, it has been found that while the ITO layer may be deposited at a rate of up to 50-100 Å per minute, or more, whenever the ITO layer is deposited on a bare substrate. However, the deposition rate may be only about 2-5 Å/minute, if the ITO is deposited directly onto an organic layer or onto a Mg:Ag surface that is typically deposited over several organic layers. Since the organic layers are highly vulnerable to damage when subjected to the beam of high energy particles that are used at the higher ITO deposition rates, higher deposition rates can cause substantial damage to the underlying organic layers, thus causing unacceptably large deterioration in the overall performance of the OLED. Whenever the ITO layer of an OLED is deposited onto such fragile organic surfaces, it would be desirable if the ITO

layer could be deposited at substantially higher deposition rates than have been possible until now.

In addition, it would be desirable if the hole injection characteristics of the hole injecting layer could be improved. It has been shown that copper phthalocyanine (CuPc) can serve as an efficient hole injection layer in conventional OLEDs, S.A. VanSlyke et al., *Appl. Phys. Lett* 69, 2160 (1996) and U.S. Pat. No. 4,720,432 and it had previously been established that 3,4,9,10-perylenetetra-carboxylic dianhydride (PTCDA) is an efficient hole transporting layer, P.E. Burrows et al., *Appl. Phys. Lett.* 64, 2285 (1994), V. Bulovic et al., *Chem. Phys.* 210, 1 (1996); and V. Bulovic et al. *Chem. Phys.* 210, 13 (1996); respectively. Furthermore, the use of PTCDA in a photodetector structure with an ITO electrode deposited on the film surface, F.F. So et al., *IEEE. Trans. Electron. Devices* 36, 66 (1989), has previously demonstrated that this material can withstand sputter-deposition of ITO with minimal degradation to its conducting properties.

Conventional displays, including LCD (liquid crystal) and conventional OLED (organic light emitting device) displays, have the additional disadvantage of not being well suited for viewing under bright ambient light. As illustrated in Fig. 21, light R emitted from a bright light source L, such as the sun, is reflected from one or more layers (primarily the metallic layers) of a conventional display D. The reflected light R interferes with the ability of a viewer V to view information bearing light I generated by the display D, thereby reducing the perceived contrast of the image generated by the display D. A need, therefore, exists for an OLED display with improved contrast which can be viewed under bright ambient light conditions.

SUMMARY OF THE INVENTION

The present invention is directed to OLEDs, and a method of fabricating such OLEDs, that comprise a heterostructure for producing electroluminescence wherein the heterostructure
5 includes a layer, between the hole transporting layer and the ITO anode layer, that protects the underlying organic layers from damage during the ITO sputter deposition process.

One of the features of the present invention is that the
10 protection layer may be used in OLEDs not only for protection of the underlying organic layers, but the protection layer may also serve as a hole injection enhancement layer. Examples of preferred embodiments of the present invention, in which the protection layer may also function as a hole injection
15 enhancement layer as disclosed in U.S. Serial No. 08/865,491, filed May 29, 1997, include PTCDA or related arylene-based compounds.

The present invention is further directed toward an improved
20 method of preparing the ITO layer of an OLED wherein, during the course of preparing the ITO layer, the deposition rate is increased from a relatively low initial deposition rate to a substantially higher deposition rate after the depositing ITO layer has reached a sufficient thickness such that damage to
25 the underlying layers is prevented. More specifically, another aspect of the present invention is directed to a vacuum deposition process in which the initial deposition rate is increased by a factor of about five- to ten-fold after a layer thickness of about 50 Å to about 200 Å is reached.
30 Still more specifically, this aspect of the present invention is directed to a process in which the initial deposition rate is about 2-5 Å/minute and the final deposition rate is at least about 50-60 Å/minute.

35 The present invention is still further directed to a high contrast, transparent organic light emitting device (TOLED) display wherein the contrast of the display is improved by minimizing the amount of light reflected from the display.

This is accomplished by the use of a display with a TOLED structure and by the arrangement of a low-reflectance absorber behind the TOLED display. TOLEDs have substantially transparent conducting layers and as such do not reflect light as do the metallic conducting layers of conventional OLEDs. The low-reflectance absorber arranged behind the TOLED display acts to absorb the light which passes through the TOLED display. The majority of the light incident on the TOLED display is absorbed by the low-reflectance absorber, with very little of the incident light reflected back to the viewer. This configuration provides improved contrast of the image displayed by the display. The display of the present invention also exhibits improved contrast for images of different colors.

The present invention is further directed to OLEDs comprised of host and dopant compounds which in combination may be used to produce emission in a relatively narrow band centered near the saturation wavelength of one of the primary colors.

Further objectives and advantages of the present invention will be apparent to those skilled in the art from the detailed description of the disclosed invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a representative IOLED for a single heterostructural device.

Fig. 2 shows the forward bias current-voltage (I-V) characteristics of 0.05 mm IOLEDs with PTCDA and CuPc protective cap layers (PCLs), which function as hole injection enhancement layers, and of a device with no PCL.

Fig. 3 shows the luminescence intensity vs. current (L-I) of the IOLEDs in Fig. 2.

Fig. 4 shows the I-V characteristics of the shape of the EL

emission spectra of IOLEDs with hole injection enhancement layers as compared to that of conventional Alq₃-based OLEDs not having the hole injection enhancement layer.

- 5 Fig. 5 shows the current vs. voltage of an OLED with and without a 60 Å PTCDA layer between an ITO anode layer and an NPD hole transporting layer.

Fig. 6 shows a cross section of an OLED containing an ITO
10 layer prepared in two stages, the first stage being prepared using a low ITO deposition rate and the second stage being prepared using a substantially higher ITO deposition rate.

Fig. 7 shows how the resistivity of 1000 Å ITO layers
15 deposited on glass with an Ar flow of 200 ("standard cm³/minute) and at a pressure of 5 mTorr and at 45 W of RF power varies as a function of the O₂ flux.

Fig. 8 shows how the absorption of 1000 Å thick ITO layers
20 deposited at 45 W of RF power varies as a function of wavelength and as a function of O₂ flux (for an Ar flow of 200 sccm, a pressure of 5 mTorr, a rate of 0.8 Å/sec and onto a glass substrate).

25 Fig. 9 shows how the I-V characteristic of a TOLED made using the higher ITO deposition rates (as shown by the small open circles) compares with the I-V characteristic of a TOLED for which the ITO layer was prepared entirely at the slower ITO deposition rate (dashed line).

30

Fig. 10 shows a representative OLED for a single heterostructural device.

Fig. 11 shows the photoluminescence (PL) spectra of
35 aluminumtris(5-hydroxy-quinoxaline), aluminum tris(5-hydroxy-quinoline) and gallium bis(5-hydroxy-quinoxaline).

Fig. 12 shows the electroluminescence spectra of OLEDs containing an emissive layer of aluminumtris(5-hydroxy-quinoxaline) with and without the inner salt of a bisphenyl-squarilium compound of formula III as a dopant.

5

Fig. 13 shows the I-V characteristics of aluminumtris(5-hydroxy-quinoxaline) with and without the inner salt of a bisphenyl-squarilium compound of formula VI as the dopant.

10 Fig. 14 shows the photoluminescent spectra of the host compounds Alq_3 and Alx_3 as compared with the absorbance spectra of the dopants: the inner salt of a bisphenyl-squarilium dye ("BIS-OH") an indigo dye compound and a fullerene compound, C_{60} .

15 Fig. 15 shows the photoluminescent spectra of the dopant compounds in solution, the inner salt of a bisphenyl-squarilium dye ("BIS-OH") (in CH_2Cl_2), an indigo dye compound (in DMSO) and C_{60} (in toluene).

20 Fig. 16 shows the electroluminescent spectra of TPD- $\text{Alq}_3/\text{C}_{60}$ devices as a function of increasing C_{60} concentration in the host Alq_3 material.

Fig. 17 shows the electroluminescent spectra of TPD- Alq_3 /(the
25 bisphenol-squarilium dye of formula XI) devices as a function of the bisphenol-squarilium dopant concentration in the Alq_3 host material.

Fig. 18 shows the electroluminescent spectra of TPD- Alx_3 /(the
30 bisphenol-squarilium dye of formula XI) devices as a function of the bisphenol-squarilium dopant concentration in the host Alx_3 material.

Fig. 19 shows the electroluminescent spectrum of the TPD- Alx_3 /
35 indigo dye compound device with a 1.7% indigo dye compound concentration.

Fig. 20 shows representative compounds according to formula XIII.

Fig. 21 shows a conventional display device under bright
5 ambient light conditions.

Fig. 22 shows a high contrast TOLED display, in accordance with the present invention, under bright ambient light conditions.

10

Fig. 23 is a cross-sectional view of a first embodiment of a high contrast TOLED display, in accordance with the present invention.

15 Fig. 24 is a cross-sectional view of a second embodiment of a high contrast TOLED display, in accordance with the present invention.

Fig. 25 is a cross sectional view of a stacked light emitting
20 device, in accordance with a first embodiment of the present invention.

Fig. 26 is a cross sectional view of a stacked light emitting
25 device, in accordance with a second embodiment of the present invention.

Fig. 27 is a cross sectional view of a stacked light emitting device, in accordance with a third embodiment of the present invention.

30

Fig. 28 is a cross sectional view of an inverted stacked light emitting device, in accordance with an embodiment of the present invention.

35 Fig. 29 shows an OLED with a distributed Bragg reflector structure.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention will now be described in detail for specific preferred embodiments of the invention, it being understood that these embodiments are intended only as
5 illustrative examples and the invention is not to be limited thereto.

The OLEDs of the present invention are comprised of a heterostructure for producing electroluminescence which may be
10 fabricated as a single heterostructure or as a double heterostructure. The materials, methods and apparatus for preparing the organic thin films of a single or double heterostructure are disclosed, for example, in U.S. Patent No. 5,554,220, which is incorporated herein in its entirety by
15 reference. As used herein, the term "heterostructure for producing electroluminescence" refers to a heterostructure that includes, for a single heterostructure, in sequence, a hole injecting anode layer, a hole transporting layer, an electron transporting layer, and a cathode layer. An
20 additional layer or layers may be present between one or more of the sequential pairs of these layers. For example, for a double heterostructure, a separate emissive layer is included between the hole transporting layer and the electron transporting layer.

25 Either the anode layer or the cathode layer may be in contact with a substrate and each electrode is connected to electrical contacts which are capable of delivering a voltage across the device causing it to produce electroluminescence from an
30 electron transporting layer, a hole transporting layer or a separate emissive layer. If the cathode layer is deposited on the substrate, the device may be referred to as having an inverted OLED (IOLED) structure. An inverted structure may also be referred to as an "OILED" structure. If the
35 heterostructure for producing electroluminescence is included as part of a stacked OLED (SOLED), one or both of the electrodes of an individual heterostructure may be in contact

with an electrode of an adjacent heterostructure. Alternatively, dependent on the circuitry used to drive the SOLED, an insulating layer may be provided between the adjacent electrodes of the OLEDs in the stack.

5 The single or double heterostructures as referred to herein are intended solely as examples for showing how an OLED embodying the present invention may be fabricated without in any way intending the invention to be limited to the
10 particular materials or sequence for making the layers shown. For example, a single heterostructure typically includes a substrate which may be opaque or transparent, rigid or flexible, and/or plastic, metal or glass; a first electrode, which is typically a high work function, hole-injecting anode
15 layer, for example, an indium tin oxide (ITO) anode layer; a hole transporting layer; an electron transporting layer; and a second electrode layer, for example, a low work function, electron-injecting, metal cathode layer of a magnesium-silver alloy, (Mg:Ag) or of a lithium-aluminum alloy, (Li:Al). In
20 the preferred embodiments of the present invention, the order of these layers may be reversed or inverted, such that the cathode layer is in direct contact with the substrate.

Preferred materials that may be used as the substrate in a
25 representative embodiment of the present invention include, in particular, glass, transparent polymers such as polyester, sapphire or quartz, or substantially any other material that may be used as the substrate of an OLED.

30 Preferred materials that may be used as the hole-injecting anode layer in a representative embodiment of the present invention include, in particular, ITO, Zn-In-SnO₂ or SbO₂, or substantially any other material that may be used as the hole-injecting anode layer of an OLED.

35 Preferred materials that may be used in the hole transporting layer in a representative embodiment of the present invention

include, in particular,

N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1-1'-biphenyl-4,4'-diamine (TPD), 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (α -NPD) or 4,4'-bis[N-(2-naphthyl)-N-phenyl-amino]biphenyl (β -NPD).

5

Preferred materials that may be used as the electron transporting layer include, in particular, tris-(8-hydroxyquinoline)-aluminum (Alq₃) and carbazole.

10 Preferred materials that may be used as the separate emissive layer, if present, include, in particular, dye-doped Alq₃, or substantially any other material that may be used as the separate emissive layer of an OLED.

15 The insulating layer, if present, may be comprised of an insulating material such as SiO₂, SiN_x or Al₂O₃, or substantially any other material that may be used as the insulating material of an OLED, which may be deposited by a variety of processes such as plasma enhanced chemical vapor
20 deposition (PECVD), electron beam, etc.

The OLEDs of the present invention may also include doped layers such as disclosed in *S.A. VanSlyke et al., Appl. Phys. Lett.* 70, 1665 (1997) and *Tang et al., J. Appl. Phys.* 64, 3610
25 (1989), which are incorporated herein by reference.

The OLEDs of the present invention have the advantage that they can be fabricated entirely from vacuum-deposited molecular organic materials as distinct, for example, from
30 OLEDs in which some of the layers are comprised of polymeric materials. Polymeric materials typically require solvent-based methods such as spin coating. Vacuum deposition methods, rather than solvent-based deposition of polymeric materials, are particularly suitable for use in fabricating
35 the OLED's of the subject invention since such methods permit integration of all the vacuum deposition steps into a single overall sequence of steps for fabricating the OLED. Such

methods, thus, do not require the use of solvents or the need to remove air sensitive layers from a vacuum chamber, such that the layers will be exposed to ambient conditions. A vacuum-deposited material is one that can be deposited in a vacuum having a background pressure less than one atmosphere, preferably about 10^{-5} to about 10^{-11} torr.

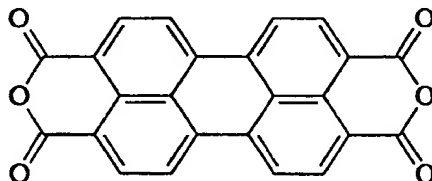
Although not limited to the thickness ranges recited herein, the substrate may be as thin as 10 μm (micrometer), if present as a flexible plastic or metal foil substrate, such as aluminum foil, or substantially thicker if present as a rigid, transparent or opaque, substrate or if the substrate is comprised of a silicon-based display driver; the ITO anode layer may be from about 500 Å (1 Å = 10^{-8} cm) to greater than about 4000 Å thick; the hole transporting layer from about 50 Å to greater than about 1000 Å thick; the separate emissive layer of a double heterostructure, if present, from about 50 Å to about 200 Å thick; the electron transporting layer from about 50 Å to about 1000 Å thick; and the metal cathode layer from about 50 Å to greater than about 100 Å thick, or substantially thicker if the cathode layer includes a protective silver layer and is opaque.

Thus, there are substantial variations in the type, number, thickness and order of the layers that are present, dependent on whether the device includes a single heterostructure or a double heterostructure, whether the device is a SOLED or a single OLED, whether the device is a TOLED or an IOLED, whether the OLED is intended to produce emission in a preferred spectral region, or whether still other design variations are used.

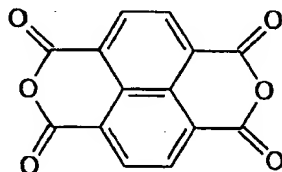
The present invention is, however, directed in particular to substantially any type of OLED structure in which a protection layer is present between the hole transporting layer and the anode layer. More specifically, the present invention is directed toward OLEDs that include a protection layer that

functions as a protective cap layer (PCL) for reducing ITO sputtering damage to the underlying organic layers during fabrication of the OLEDs. The present invention is further directed to the OLEDs having the enhanced hole injection efficiency properties observed for OLEDs containing such a protection layer. The enhanced hole injection efficiency is characterized by having a higher injected current at a given forward bias, and/or a higher maximum current before device failure. A "hole injection enhancement layer" is, thus, a layer that may be characterized as a layer that produces a current that is at least about 10% higher, typically about 50-100% higher or still higher, than a similar device that lacks such an additional layer. Such layers are believed to provide improved matching of the energy levels of the adjacent layers in a manner that results in enhancement of hole injection.

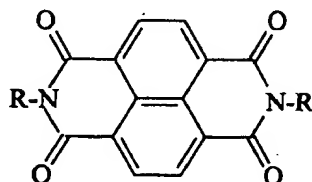
The protection layer, which may also function as a hole injection enhancement layer, may be formed, for example, by deposition of a phthalocyanine compound or of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA):



bis(1,2,5-thiadiazolo)-p-quinobis(1,3-dithiole) (BTQBT), or other suitable, rigid organic materials, such as shown by the following compounds:

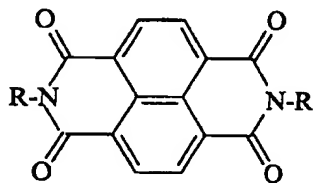


1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA);

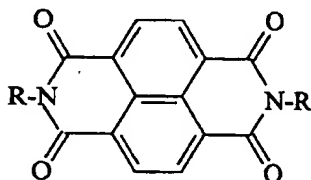


where R = H, alkyl or aryl;

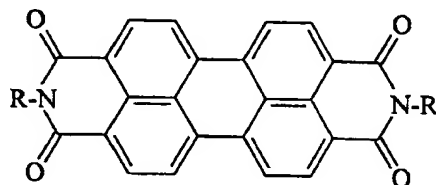
5



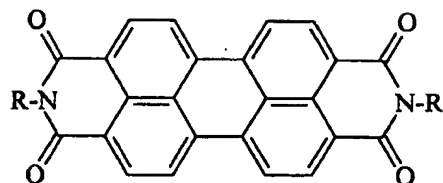
where R = H, (1,4,5,8-naphthalenetetracarboxdiimide);



10 where R = CH₃, (N,N'-dimethyl-1,4,5,8-naphthalenetetracarboxdiimide);

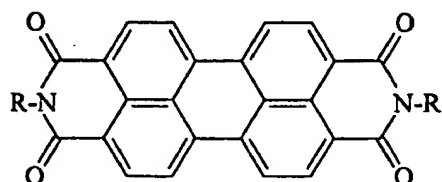


where R = H, alkyl or aryl;

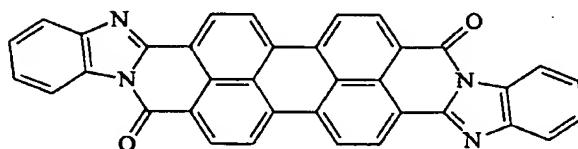


where R = H, (3,4,9,10-perylenetetracarboxylic diimide);

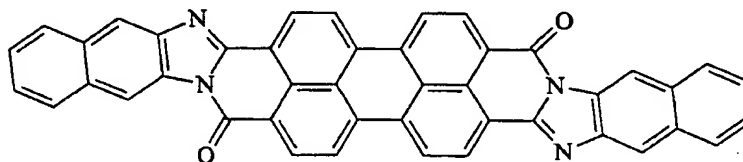
5



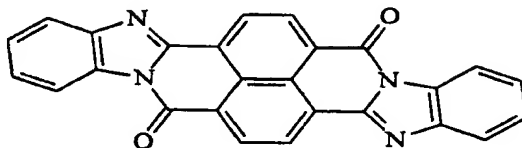
where R = CH₃, (N,N'-dimethyl-3,4,9,10-perylenetetracarboxylic diimide);



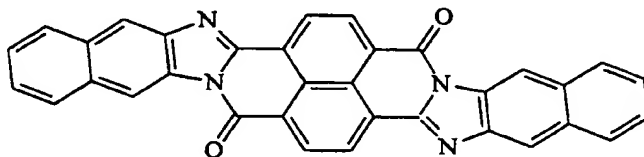
10 having a CA index name, bisbenzimidazo[2,1-a:1',2'-b']anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-10,21-dione;



having a CA index name, bisnaphth[2',3':4,5]imidazo[2,1-a:2',1'-a']anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-10,21-dione;



- 5 having a CA index name, bisbenzimidazo[2,1-b:2',1'-i]benzo[lmn][3,8]phenanthroline-8,1-dione;



- having a CA index name,
10 benzo[lmn]bisnaphth[2',3':4,5]imidazo[2,1-b:2'1'-I][3,8]phenanthroline-9,20-dione.

- A substituted derivative of any one of these perylene,
naphthalene, isoquinoline, phthalocyanine, or phenanthroline
15 based compounds, or family of compounds, may also be used
while remaining within the scope and spirit of the present
invention.

- In one of the preferred embodiments, the cathode is deposited
20 as the bottom layer on the substrate onto which the inverted
OLED is deposited. Such an inverted OLED has the advantage
that it can be fabricated entirely from vacuum-deposited
molecular organic materials as distinct, for example, from
OLEDs in which some of the layers are comprise of polymeric
25 materials, which cannot be readily deposited using vacuum
deposition techniques. While a protective layer was typically
not necessary in inverted polymer-containing OLEDs since the
glass transition temperature (T_g) of polymer materials is

typically much higher and, thus, more resistant to damage induced by ITO sputtering, than the T_g of molecular (non-polymeric) organic materials, such inverted polymer-containing OLEDs cannot be readily fabricated using the vacuum deposition technology that is readily available for preparing OLEDs. The protective cap layer is typically comprised of a crystalline organic layer that protects the underlying hole conducting material from damage incurred during sputter deposition of the ITO anode.

10

The present invention is, thus, directed to OLEDs having organic layers that can be fabricated entirely from vacuum-deposited materials. Moreover, the present OLEDs are comprised of vacuum-deposited molecular organic materials that contain a crystalline organic layer that may serve not only to protect the underlying hole transporting material from damage incurred during sputter deposition of the ITO anode but such a layer may also serve as a hole injection enhancement layer.

15

20 The forward bias current-voltage (I-V) characteristics of 0.05 mm² IOLEDs with PTCDA and CuPc PCLs, which are shown in Fig. 2, show that these characteristics are similar to previously reported conventional IOLEDs, where trap limited conduction was observed, Z. Shen et al., *Jpn. J. Appl. Phys.* 35, L401 (1996), P.E. Burrows *J. Appl. Phys.* 79, 7991 (1996), ($I \propto V^{(m+1)}$). For the IOLEDs, $m = 8$ independent of the details of the particular device structure or PCL thickness. The EL brightness at a current density of 10 mA/cm² was between 40 and 100 cd/m² for all devices, independent of details of the HTL, PCL or anode structure. The IOLEDs, whose characteristics are presented in Fig. 2, are a representative sample of devices with different thicknesses of PTCDA or CuPc. The operating voltage of IOLEDs employing CuPc as the PCL was independent of CuPc thickness between 40 Å and 170 Å. In contrast, the operating voltage of PTCDA-protected IOLEDs abruptly decreased by 1.5 V as the PTCDA thickness increased from 40 Å to 60 Å. The voltage drop across the PCL is typically small compared to

30

35

that across the rest of the device, since PTCDA and CuPc are both thinner and more conductive. Therefore, the abrupt change in the I-V characteristics reflects a change in the hole injection efficiency from the ITO contact.

5 While not intending to be limited to the precise theory of how the hole injection efficiency is enhanced for OLEDs containing a PCL, the enhancement is believed to be partly due to the reduced damage of the vacuum deposited hole transport layer
10 during deposition of the ITO layer and partly due to a reduced barrier for hole injection from ITO into the hole injection enhancement layer. The ITO sputter deposition typically inflicts film damage to the top-most organic layer. This damage results in only a 30% yield out of 15 devices with no
15 PCL, as compared to 100% yield for devices with either a PTCDA or CuPc PCL. The abrupt increase in the operating voltage for IOLEDs with < 40 Å thick PTCDA layers occurs when the thickness of the damaged region is comparable to the PCL thickness. At this point, further deposition of ITO degrades
20 the TPD which becomes directly exposed to the sputtering plasma.

The presence of the PCL also influences the maximum drive current before device breakdown (I_{\max}), where I_{\max} for an IOLED
25 with no PCL is only 10% of that obtained for IOLEDs with either a PTCDA or CuPc PCL. The differences in I_{\max} are evident in both Figs. 2 and 3, where all IOLEDs were driven at continuously higher currents until device breakdown occurred.

30 The PCL is, therefore, shown herein to protect the underlying organic materials, to decrease the IOLED operating voltage, and to increase I_{\max} of the IOLEDs prepared containing the PCL. A similar decrease in the operating voltage was previously observed for conventional OLEDs with a CuPc coated
35 ITO anode, S.A. VanSlyke et al., *Appl. Phys. Lett* 69, 2160 (1996). This is believed to be due to a reduced energy barrier to hole injection from the ITO into CuPc as opposed to

the energy barrier between the ITO and the HTL. The lowest transition voltage (i.e. the voltage at which ohmic conduction and trap limited conduction are equal) was achieved for IOLEDs with $> 100 \text{ \AA}$ thick PTCDA PCLs. These results show an enhanced hole injection efficiency as compared with IOLED devices not including the PCL.

Fig. 3 shows the light intensity vs. current (L-I) response of the IOLEDs in Fig. 2. The external EL quantum efficiency of the protected IOLEDs was $\eta = (0.15 \pm 0.01)\%$ vs. $\eta = (0.30 \pm 0.02)\%$ for the unprotected devices. This difference is believed to be due in part to absorption by the PCL, since both CuPc and PTCDA exhibit a strong absorption at the peak Alq_3 emission wavelength of 530 nm. For example, η decreases by 25% as the CuPc PCL thickness increases from 40 \AA to 170 \AA . Similarly, η for PTCDA-protected IOLEDs decreases by 25% with an increase in PTCDA film thickness from 10 \AA to 120 \AA , consistent with PTCDA absorption. The origin of the remaining difference in η between IOLEDs with and without a PCL is not understood, although it is believed that defects at the PTCDA/ITO interface may scatter a fraction of the emitted light back into the PTCDA where it can experience further absorption. A different PCL material, some of which are described above, which is transparent to Alq_3 emission is thus expected to increase the IOLED efficiency somewhat. The shape of the EL emission spectra of IOLEDs with PCLs is similar to that of conventional Alq_3 -based OLEDs (Fig. 4). The IOLED spectrum with a 60 \AA thick PTCDA PCL is slightly broadened due to the PCL absorption.

The results shown in Fig. 5 show that a surface-emitting, or inverted organic LED (IOLED) with a cathode as a bottom contact and using a novel anode comprised of an organic hole-injecting PCL and a transparent, sputter-deposited ITO thin film could produce enhanced hole injection efficiency as compared with IOLEDs lacking such a PCL. The IOLED can be grown on top of any smooth substrate to which the cathode will

adhere, including opaque substrates such as Si and metal foils. The IOLED I-V characteristics and EL spectra were similar to that of conventional OLEDs, while the operating voltage is higher and efficiency somewhat decreased,
5 indicating the need for further optimization of the device contacts.

Still another aspect of the present invention is directed to an alternative method for reducing or preventing the ITO
10 sputtering damage. This method may be used in place of or in addition to using the protection layer. In this method, the ITO layer is deposited initially at a relatively low ITO deposition rate so as to avoid causing damage to the
underlying organic layers and then the ITO layer is deposited
15 at a relatively high rate, so as to reduce the time required to fabricate the OLEDs. In particular, during the initial stages of the ITO deposition process, when substantial damage to the OLED surface may occur, the ITO deposition rate is preferably only about 2-5 Å/minute. However, after the
20 growing ITO layer reaches a certain threshold thickness that is sufficient to protect the underlying layer or layers, the deposition rate may be increased several fold, preferably, to a deposition rate that is at least 5 to 10 times higher than the initial deposition rate. Though the improved ITO
25 deposition method is preferably used in combination with a protection layer, the improved ITO deposition method may in some cases be used without using the protection layer.

For the RF power supply used to prepare the ITO layers
30 according to the subject method, which was an Advanced Energy ATX-600 RF power supply, Fort Collins, Colorado, USA, the power settings may be varied from about 1W-7W for the low ITO deposition rates and from about 20W-40W for the higher ITO deposition rates. Thus, in going from the low ITO deposition
35 rate up the higher ITO deposition rate, there may be an increase in the power settings of the RF power supply from as much as about a 3-fold increase up to about a 40-fold

increase. Preferably, the increase is such as to produce an increase in the ITO deposition rate of at least from about a 5-fold increase up to about a 10-fold increase.

- 5 The underlying layer or layers may be a thin and relatively fragile Mg:Ag cathode layer, an organic layer that is under the Mg:Ag cathode layer, and/or an organic layer, such as a hole transporting layer, onto which the ITO layer is directly deposited, for example, whenever an IOLED is being fabricated.
- 10 As described herein, a low ITO deposition rate is one for which no practically discernible damage to a fragile layer can be detected and a high ITO deposition rate is one for which discernible damage to a fragile layer can be detected.
- 15 A threshold thickness of ITO that is sufficient to protect the underlying layer or layers from damage during the ITO deposition process, herein referred to as a "protective ITO layer," is one for which no practically discernible difference is observed in the I-V characteristics for OLEDs prepared
- 20 using the higher ITO deposition rates, as compared with OLEDs wherein the ITO layer is prepared using only the low, non-damaging, ITO deposition rates. No practically discernible difference in I-V characteristics is one for which, over the range of voltages applied across a particular OLED structure,
- 25 the voltage required to obtain a particular current is within about 20% of the value that can be observed for that particular OLED structure whenever the ITO is deposited only at the low, non-damaging, ITO deposition rates.
- 30 While the threshold thickness of the growing layer of ITO that is required to protect the underlying layers may vary depending on the actual materials that are in the underlying layers, this threshold thickness is preferably about 50 to 200 Å, and more preferably about 50 to 100 Å, before substantially
- 35 increasing the deposition rate. While the maximum rate that may be used without causing damage may also vary over a substantial range, also depending on the actual materials

being coated, the deposition rate may be increased from about 2-5 Å/minute to at least about 50 to about 60 Å per minute. Programming the deposition process so as to gradually and continuously increase the ITO deposition rate throughout the process or, alternatively, to continuously increase the ITO deposition rate only after a certain threshold ITO thickness is reached also falls fully within the scope and spirit of the present invention. In such cases, whenever the ITO deposition rate is increased gradually and continuously, it is to be understood that the threshold thickness that is sufficient to function as the protective ITO layer may be somewhat thinner than that required whenever the ITO deposition rate is abruptly increased to a substantially higher ITO deposition rate.

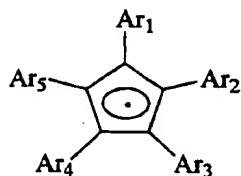
The performance of the OLEDs prepared using the present invention may be evaluated by comparing the I-V characteristics of OLEDs made using the accelerated ITO deposition rate as compared with OLEDs prepared using a single ITO deposition rate throughout the ITO deposition process. It was discovered that OLEDs prepared using the present accelerated deposition rate method could be made with I-V characteristics having no practically discernible difference from the I-V characteristics of an OLED in which the deposition rate was kept at a low deposition rate throughout the ITO deposition process.

In the preferred embodiments of the present invention, the ITO layer is sputtered using an RF power source onto the target in the presence of an oxygen flux that is selected to provide the desired combination of transparency and electrical resistivity values for a given ITO layer thickness. The actual oxygen flux that is selected may vary widely depending on the characteristics of the specific fabrication system used and may be evaluated in terms of the absorption of visible radiation by the ITO layer. In particular, it is preferable that the absorption of visible radiation, which varies as a

function of wavelength over the visible region of the spectrum, be such as to produce a total light transmission, for the ITO layers made using the accelerated deposition rates, comparable to that for ITO coatings prepared at the
5 lower ITO deposition rates.

The oxygen flux may vary over the range from about 0.35 to about 0.50 sccm ("standard cm³/minute") for the higher ITO deposition rates and from none at all up to about 0.2 sccm,
10 preferably, about 0.1 sccm, for the much lower ITO deposition rates. Using these criteria to evaluate the performance of the ITO layers prepared using the subject method, it has been found that an increase in the ITO deposition rate of at least
15 ten-fold could be used to produce ITO coatings having I-V characteristics nearly identical to coatings prepared using only the lowest ITO deposition rates. Such an increase is typically produced by using a ten-fold increase in the RF power settings.

20 In a further aspect of the present invention, the electron transporting layer of OLEDs made according to the present invention may be comprised of an organic free radical, which may be prepared in a manner that is suitable for fabricating the electron transport layer of an OLED. In a representative
25 embodiment of the present invention, the electron transporting material is represented by the chemical structure, Cp^{Ar}·, of formula (I):



(I)

30 which is herein referred to as multi-aryl-substituted cyclopentadienyl free radical, wherein each Ar-group, Ar₁, Ar₂,

Ar₃, Ar₄ and Ar₅, is hydrogen, an alkyl group or an unsubstituted or substituted aromatic group. Although the term "Ar-group" may typically be used to refer only to aryl groups, the term is used herein to include hydrogen or an alkyl group even though, preferably, at most only one of the Ar-groups is an alkyl group or hydrogen, with the remainder being aromatic groups, and, most preferably, all of the Ar-groups being aromatic groups. The aromatic groups may be independently selected to be the same or different, one from the other, with the total number of compounds that may be embraced by formula I being limited only insofar as they may be suitable for use in preparing an electron transporting layer and insofar as it is chemically practical to prepare such compounds. An organic free radical compound is herein defined to be suitable for use as an electron transporting material if the carrier mobility of the electron transporting layer has a value of at least 10^{-6} cm²/V sec.

The unsubstituted or substituted aromatic groups may be, for example, phenyl groups; groups having fused phenyl rings, such as naphthyl; or aromatic heterocyclic groups such as pyridyl or thiophenyl.

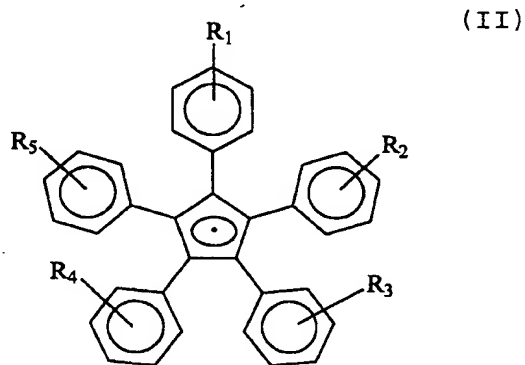
Each aromatic group may be, independently of the other aromatic groups, unsubstituted or substituted with one or more substituent groups. The substituent group, or groups, may be an electron donor group, an electron acceptor group or an alkyl group.

For those compounds which function not only as an electron transporting material but also serve as an emissive material, the unsubstituted or substituted aromatic group may be selected so as to adjust the spectral emission characteristics in a manner such as to produce a desired color, as characterized, for example, by using the X-Y chromaticity coordinates of the CIE colorimetric system. For example, it is known that substantial changes in the emission spectra of a

phenyl-containing compound may be produced dependent on whether the phenyl group is unsubstituted or is instead substituted in the ortho or para position with an electron donor group or an electron acceptor group. In addition to
5 being selected to adjust the emission characteristics, the donor and acceptor groups may also be selected to affect the degree of intermolecular interaction and, thus, carrier mobility. Moreover, such substituents may also be selected so as to adjust the reduction potential of the organic free
10 radicals, that is, the energy required to reduce the free radicals, thus converting the free radicals to the anions of the free radical. By suitably selecting the substituents to produce a readily accessible reduction potential, the carrier mobility and/or the carrier trap depth may be favorably
15 altered, such that stable organic free radicals may be produced that have an overall combination of electron-transporting and electron-emissive properties that is particularly suitable for use as an electron transporting layer.

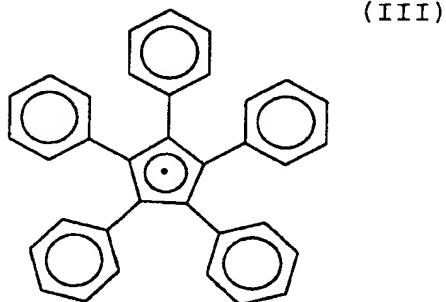
20

Still more specifically, in a preferred embodiment, the organic free radical is a pentaphenylcyclopentadienyl radical, Cp^\bullet of formula (II):

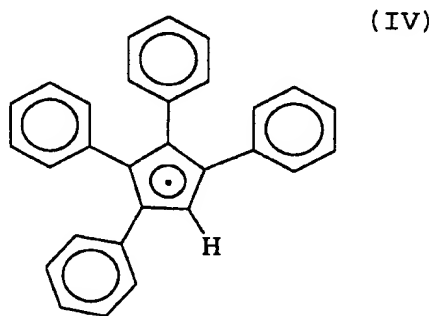


wherein each aryl group of formula (I) is defined in formula (II) as being a single phenyl group that may be unsubstituted, or substituted with the substituents R_1 , R_2 , R_3 , R_4 and R_5 , respectively, wherein each R-group represents independently
5 from the other R-groups, one or more of an electron donor group, an electron acceptor group or an alkyl group.

As a specific illustrative embodiment of the present invention, the organic free radical may be the unsubstituted
10 Cp^\bullet , as represented by formula (III):



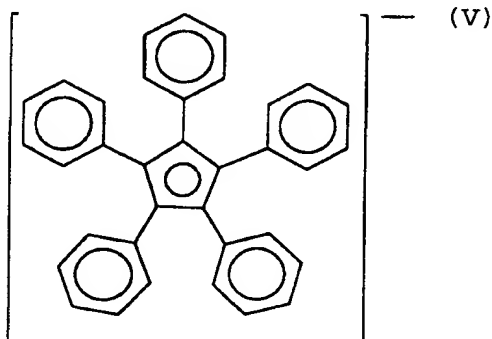
As still another specific illustrative embodiment of the present invention, the organic free radical may be the
15 tetraphenylcyclopentadienyl free radical of formula (IV),



and further-substituted variations thereof, for example, wherein the hydrogen shown in formula (IV) may be replaced by an alkyl group.

- 5 While not intending to be limited by the theory of the invention for the representative embodiments of the specific organic free radicals as disclosed herein, it is believed that the effectiveness of the Cp^{Ar} free radical as an electron transporting material in the ETL of an OLED may be based on a
- 10 combination of properties. These include the presence of a sterically shielded central cyclopentadienyl ring, which can form an unusually stable organic free radical because of the substantially complete steric shielding of the cyclopentadienyl ring; the ability of the cyclopentadienyl
- 15 free radical to readily form an anion, which acting together with the free radical, serves as an electron carrier; and the strong aromatic character of the cyclopentadienyl anion, which results in strong overlap of the π -orbitals of the anion with the π -orbitals of the phenyl substituents, thus enhancing the
- 20 election mobility that promotes effectiveness of the material as an electron carrier. The present invention has the further feature that the substituents that are included in the organic free radicals may be selected so as to alter the emissive spectra and the reduction potential of the free radical in a
- 25 manner so as to produce an overall combination of electron-transporting and electron-emissive properties that is particularly suitable for use as an electron transporting layer.
- 30 The present invention is thus directed to electron transporting materials suitable for use in the electron transporting layer of an OLED, wherein the electron transporting material is comprised of a stable organic free radical having a readily accessible reduction potential
- 35 between the stable organic free radical and the anion formed from the radical, for example, the pentaphenylcyclopentadienyl

free radical, Cp^\bullet , of formula (III) and the pentaphenylcyclopentadienyl anion of formula (V):



5 A ready accessible reduction potential leads to suitable electron conduction through the electron transporting layer, wherein suitable electron conduction is herein defined to mean an electron conduction based on having an electron mobility of at least about $10^{-6} \text{ cm}^2/\text{V sec}$.

10

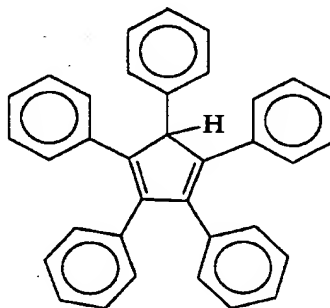
An electron transporting layer comprised of the Cp^\bullet free radical provides a further advantage in that the electron transporting material may, in some cases, also function as an emissive material in the OLED. Whenever the electron
 15 transporting material also serves as an emissive material, the OLED may be fabricated using a single heterostructure. If the electron transporting material does not also serve as an emissive material, the OLED may be fabricated from a single heterostructure in which the hole transporting layer is the
 20 emissive layer or from a double heterostructure.

The present invention is further directed toward a novel method for preparing the Cp^\bullet free radical in bulk form as a thin layer of electron transporting material having a high
 25 electron mobility and a high electron carrier density, wherein the electron transporting layer is included in a multi-layer

structure, in particular, a heterostructure for producing electroluminescence. It is believed that no prior art electron transporting materials have been disclosed which are comprised of an organic free radical. Thus, while the present invention is directed toward use of a multi-aryl-substituted cyclopentadienyl free radical, or more specifically, a multi-phenyl-substituted cyclopentadienyl free radical, or still more specifically, a pentaphenylcyclopentadienyl free radical as a species representing the preferred embodiment, it is to be understood that the present invention is generally directed toward any organic free radical that may be contained in an electron transporting layer as an electron transporting material having an electron mobility of at least 10^{-6} cm²/V sec.

15

In addition to being a free radical, the Cp[•] free radical differs from the pentaphenylcyclopentadiene itself, Cp[•]H:



20

in that Cp[•]H has been reported to be a blue emitting material when used in OLEDs, C. Adachi et al., *Appl. Phys. Lett.*, vol. 56, 799-801 (1990), whereas a film of the pentaphenylcyclopentadienyl free radical has been observed and reported to have a purple color, M.J. Heeg et al., *J. Organometallic Chem.*, vol. 346, 321-332 (1988).

Furthermore, the Cp[•] free radical differs from Cp[•]H in that the latter is not readily reduced. Reduction of Cp[•]H would have to be followed by loss of H⁺ to give the stable anionic form, which is not energetically feasible. In particular, whereas

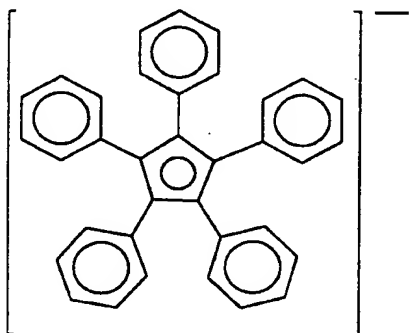
30

there is no reason to expect, based on these differences, that $\text{Cp}^\bullet\text{H}$ would have good carrier transport properties at all, the Cp^\bullet free radical is capable of being especially well suited for this purpose.

5

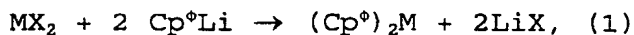
Another feature of the present invention is based on the fact that, while it is typically difficult to prepare and store Cp^\bullet by conventional methods, the Cp^\bullet free radical material of the present invention may be readily prepared *in vacuo* from air-stable precursor complexes. The metallocene complexes of
 10 pentaphenylcyclopentadiene, such as $(\text{Cp}^\bullet)_2\text{M}$, where $\text{M} = \text{Fe}, \text{Ru}, \text{Sn}, \text{Ge}$ or Pb , may be prepared as disclosed in Heeg et al. These materials can be prepared from the metal salts and the Cp^\bullet anion, $[\text{Cp}^\bullet]^-$,

15



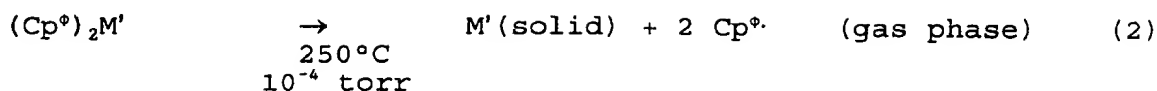
as illustrated by the following equation:

20



where $\text{M} = \text{Fe}, \text{Ru}, \text{Sn}, \text{Ge}$ or Pb ; and $\text{X} = \text{halide}$ or acetate . Each of these complexes are air stable complexes. However,
 25 the Ge and Pb complexes are not thermally stable. Attempted sublimation of the Ge and Pb complexes at 250°C and about 10^{-4} torr was reported to lead to formation of a metal mirror and sublimation of the gaseous Cp^\bullet free radical species, as shown by the following equation:

30



- 5 The purple films which are deposited from the gas phase organic free radical, Cp^\bullet , are comprised only of the Cp^\bullet free radical material, according to Heeg et al.

The present invention is directed toward using such precursor
10 materials and such methods to prepare electron transporting layers that may be used in substantially any type of multi-layer structure that includes an electron transporting layer. In particular, the free-radical-containing, electron transporting layer may be included, for example, in the multi-
15 layer structure of a light emitting device, that is, in a heterostructure for producing electroluminescence. The present invention is, thus, directed to incorporating the subject electron transporting layers into multi-layer structures wherein the electron transporting layer is in
20 electrical contact with a hole transporting layer.

The stable organic free-radical-containing materials are intended to provide benefits and advantages that are uniquely suited for use as an electron transporting material, when such
25 free-radical-containing materials are incorporated into a multi-layer structure as the electron transporting layer. While it is intended, in the more preferred embodiments of the present invention, that the electron transporting layer be comprised predominantly of an organic free radical, or even,
30 in some cases, be directed to electron transporting layers consisting essentially of organic free radicals, it is also contemplated that layers containing free radical materials that have undergone dimerization, even substantial dimerization, may also serve as effective electron
35 transporting materials, and are, therefore, also contemplated to fall within the scope of the present invention.

In fact, while the electron transporting layer be comprised

predominantly, if not completely, of an organic free radical material, the present invention may embrace any electron transporting layer that includes an organic free radical material for which it can be shown that the presence of the
5 organic free radical contributes to the electron-transporting characteristics of the electron transporting layer. For example, the layer may be comprised of organic free radical materials that are embedded in a matrix of non-free-radical, but still electron-transporting, material. An electron
10 transporting layer comprised predominantly of an organic free radical is herein defined as a layer in which the organic free radical is the major component of the electron transporting layer.

15 In the preferred embodiments of the present invention, the Ge (decaphenylgermanocene) or Pb (decaphenyl-plumbocene) complex of pentaphenylcyclopentadienyl is used as the source for preparing the thin layers of Cp^0 in a vacuum deposition system.

20

The present invention is further directed to OLEDs in which dopant compounds may be included in the emissive layer. A dopant capable of shifting the emission wavelength of an emissive layer comprised only of a host compound is added to
25 the host compound in an amount effective to shift the wavelength of emission so that the LED device preferably emits light that is perceived by the human eye to be close to one of the primary colors. Although it is recognized that characterization of color perception is a subjective exercise,
30 a quantitative chromaticity scale has been developed by the Commission Internationale de l'Eclairage (International Commission of Illumination), otherwise known as the CIE standard. According to this standard, a saturated color may be represented by a single point, with specific quantitative
35 coordinates according to the defined axes of the chromaticity scale. It will be appreciated by one of skill in the art that such a single point on the CIE scale would represent a

standard or a goal that, in practical terms, is difficult, but fortunately, unnecessary, to attain.

In the preferred embodiments of the present invention in which
5 the OLED produces a primary color, the dopant is incorporated
into a host compound so that the OLED emits light that is
perceived by the human eye to be close to a saturated primary
color. Through the practice of the present invention, it is
intended that OLEDs be constructed which can be characterized
10 by an emission that is close to an absolute (or saturated)
chromaticity value, as that would be defined by the CIE scale.
Furthermore, LED's utilizing the materials of the present
invention are also intended to be capable of a display
brightness that can be in excess of 100 cd/m² although somewhat
15 lower values, perhaps as low as 10 cd/m², may be acceptable in
certain cases.

The host compounds as defined herein are compounds which can
be doped with dopants to emit light with the desired spectral
20 characteristics. The term "host" is used to refer to the
compound in the emissive layer that functions as the component
which receives the hole/electron recombination energy and then
by an emission/absorption energy transfer process, transfers
that excitation energy to the dopant compound, which is
25 typically present in much lower concentrations. The dopant
may then relax to an excited state having a slightly lower
energy level, which preferentially radiates all of its energy
as luminescent emission in a desired spectral region. A
dopant that radiates 100% of the dopant's excited state
30 excitation energy is said to have a quantum efficiency of
100%. For host/dopant concentrations which are to be used in
a color tunable SOLED, preferably most, if not all, of the
host's excitation energy is transferred to the dopant which in
turn radiates, perhaps from a lower energy level, but with a
35 high quantum efficiency, to produce visible radiation having a
desired chromaticity.

As the term host compound is used herein, it will be appreciated that such compounds can be found in either an electron transporting/emissive layer of a single heterostructure OLED device or in the separate emissive layer of a double heterostructure device. As will be recognized by one of skill in the art, use of the dopant species such as disclosed herein makes it possible to extend not only the range of colors emitted by the OLED, but also to extend the range of possible candidate species for host and/or dopant compounds. Accordingly, for effective host/dopant systems, although the host compound can have a strong emission in a region of the spectrum where the dopant species strongly absorbs light, the host species preferably does not have an emission band in a region where the dopant also emits strongly. In structures where the host compound also functions as a charge carrier, then additional criteria such as redox potential for the species also becomes a consideration. In general, however, the spectral characteristics of the host and dopant species are the most important criteria.

The amount of dopant that is present is that amount which is sufficient to shift the emission wavelength of the host material as close as possible to a saturated primary color, as that would be defined according to the CIE scale. Typically, the effective amount is from about 0.01 to 10.0 mol %, based on the emitting layer. The preferred amount is from about 0.1 to 1.0 mol %. The primary criterion for determining an appropriate doping level is the level which is effective for achieving an emission with the appropriate spectral characteristics. By way of example, and without limitation, if the amount of dopant species is at too low a level, then emission from the device will also comprise a component of light from the host compound itself, which will be at shorter wavelengths than the desired emission from the dopant species. In contrast, if the level of dopant is too high, emission efficiencies could be adversely affected by self-quenching, a

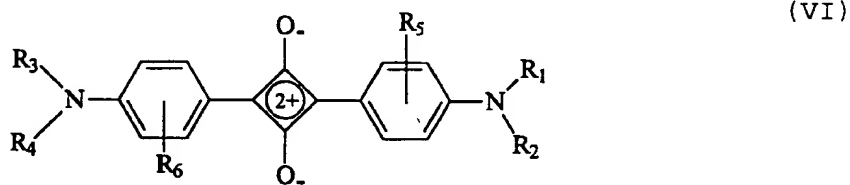
net non-emissive mechanism. Alternatively, too high levels of the dopant species could also adversely affect the hole or electron transporting properties of the host material.

- 5 A further embodiment of the present invention is directed, in particular, to an emissive layer containing a host material of a metal complex of (5-hydroxy)quinoxaline,



- 10 wherein M is Al, Ga, In, Zn or Mg, with $n = 3$, if M is Al, Ga or In and $n = 2$, if M is Zn or Mg.

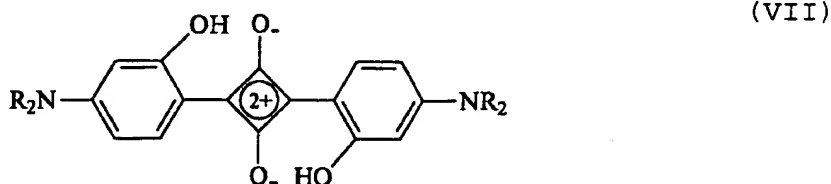
A still further embodiment of the present invention is directed to dopant materials comprised of an inner salt having
15 the chemical structure of formula VI:



- wherein R_1 , R_2 , R_3 and R_4 are, independently of each other, an unsubstituted or substituted alkyl, aryl or heterocycle (for
20 example, a pyrrole), and R_5 and R_6 are, independently of each other, an unsubstituted or substituted alkyl, aryl, OH or NH_2 . Such compounds are herein referred to as bisphenyl-squarilium compounds.

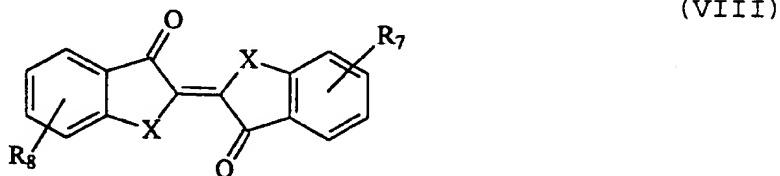
Still more specifically, one of the embodiments of the present invention is directed to dopant materials comprised of an inner salt of a compound having the chemical structure of formula VII:

5



wherein R = an alkyl. Such compounds are herein referred to as squarilium dyes.

- 10 Another embodiment of the present invention is directed to dopant materials comprised of an indigo dye compound having the chemical structure of formula VIII:



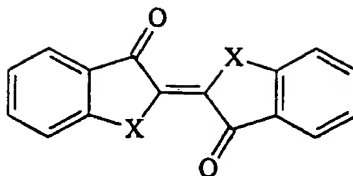
- 15 wherein X = NH, NR₉, S, Se, Te, or O, wherein R₉ is alkyl or phenyl, and R₇ and R₈ are, independently of each other, an unsubstituted or substituted alkyl or aryl group, or a π-electron donor group such as -OR, -Br, -NR₂, etc. or a π-electron acceptor group such as -CN, -NO₂, etc.

20

Still more specifically, another of the embodiments of the present invention is directed to dopant materials comprised of an indigo dye compound having the chemical structure of formula IX:

25

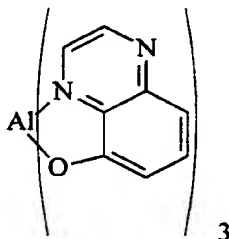
(IX)



wherein X = NH.

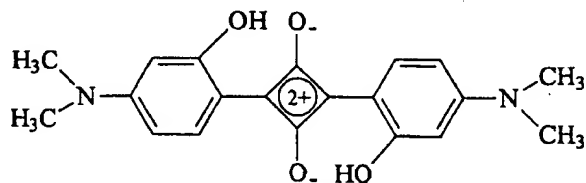
Still another embodiment of the present invention is directed
 5 to dopant materials comprised of a fullerene compound, for
 example, the C₆₀ fullerene compound.

As an illustrative example of the present invention, the host
 compound, is preferably comprised of the compound of formula V
 10 wherein M = Al and n = 3 aluminum tris(5-hydroxy-quinoxaline),
 ("Alx₃"):



(X)

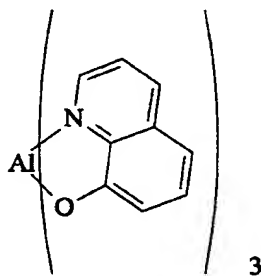
and the dopant compound is preferably comprised of the
 squarilium dye compound of formula XI, 1,3-bis[4-
 15 (dimethylamino)-2-hydroxyphenyl]-2,4-
 dihydroxycyclobuteneolylum dihydroxide, bis(inner salt) [63842-
 83-1]:



(XI)

Vacuum-deposited, single heterostructural OLEDs may be made having an electron transporting layer comprised of a host compound of formula X and a dopant compound of formula XI, wherein the OLED has current-voltage (I-V) characteristics, UV-visible, photoluminescence and electroluminescence properties that are particularly suitable for OLEDs. It is believed that the effectiveness of this particular host/dopant combination is based on achieving a high level of energy transfer from the host to the dopant. Such a high level of energy transfer, for suitably matched hosts and dopants, can lead to more efficient electroluminescence as compared to when the host compound is used alone.

While not intending to be limited by the theory of the invention for the representative embodiments as disclosed herein, as a means of illustrating how such combinations of host and dopant compounds can be selected and matched to provide efficient electroluminescence (EL), the photoluminescence (PL) of the host Alx_3 compound, with and without the dopant dye compound, may be compared with Alq_3 :



which was also prepared with and without the dopant compound.

The PL of these compounds may be measured using standard techniques, for example, by immersing the compounds in a

solvent, exposing them to a photoexcitation source and measuring the photoluminescence spectrum as a function of wavelength using equipment such as is available from Photon Technology International, in Somerville, New Jersey, USA.

5

The PL spectrum of Alq₃, Alx₃ and Gax₃ is shown in Fig. 11. The Alx₃ produces an orange photoluminescence with a maximum at about 620 nm, which is significantly red shifted relative to Alq₃, which has a PL maximum at about 515 nm. It is believed
10 that this large red shift can be significant in helping to achieve the high level of energy transfer from the host Alx₃ compound to the red fluorescent dye dopant. The EL spectra of OLEDs prepared with an un-doped and doped Alx₃ layer are shown in Fig. 12. Whereas the undoped host material has an EL
15 spectrum that is slightly red shifted as compared with the PL spectrum of the host material, the maximum occurs in a wavelength region that still has an orange appearance, as characterized, for example, by the standard CIE colorimetric system ($x = 0.565$, $y = 0.426$). However, when this host
20 material is doped with the inner salt dye of formula XI, the EL spectrum has a maximum in a wavelength region that is significantly shifted toward the red ($x = 0.561$, $y = 0.403$).

Further embodiments of the present invention are directed to
25 OLEDs having an emissive layer containing a dopant comprised of an indigo dye compound of formula VIII or of a fullerene compound. Without in any way limiting the scope of these classes of compounds, species of these classes of compounds are represented by the indigo dye compound of formula IX and
30 the fullerene compound C₆₀. The absorbance spectra of these compounds, as shown in Fig. 14, together with the bisphenol squarilium compound of formula XI, show that these compounds have absorption bandwidths which are suitably matched to accept the photoluminescence from the host compounds Alx₃ and
35 Alq₃.

The photoluminescent spectra of these dopants, as shown in Fig. 15, show that each of these compounds produces luminescence in or toward the red region of the visible spectrum. Furthermore, as illustrated by the
5 electroluminescent spectra of OLEDs incorporating the fullerene or squarilium dye dopants in a single heterostructural device using Alx₃ or Alq₃ as the host material, each of these compounds is shown to be capable, at sufficient dopant concentrations, of having the excitation
10 energy completely transferred from the host, see Figs. 16, 17, 18. Part of that energy is then radiated as electroluminescence by the dopant. The capacity for a dopant to replace substantially all of the emission of the host compound with that of the dopant is of particular benefit, for
15 example, in a color tunable SOLED. In such devices, which have more than one color-emitting layer, it is desirable to have each layer with its own well-defined chromaticity and with a spectral emission that does not overlap the spectral emission of any other layer.

20 The electroluminescent emission of an OLED containing the representative indigo dye compound is shown to have an emission band having a maximum near 650 nm (with CIE values, x=0.693 and y=0.305), which produces a saturated red
25 appearance.

The Zn and Mg derivatives of (5-hydroxy)quinoxaline have also been prepared and found to produce PL spectra nearly identical to that observed for Alx₃. In view of the effectiveness of
30 Alx₃ as a host material for red-emitting dopants wherein there is also a good energy match, such PL spectra show that the Zn and Mg derivatives may also be useful as host materials for suitably selected red-emitting dopants.

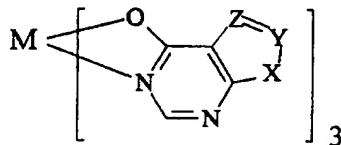
35 The Ga derivative of (5-hydroxy)quinoxaline has also been prepared and found to have the PL emission spectrum as shown in Fig. 11. These results show that the Ga analog may be

effective not only as a doped emissive material, but also as an un-doped material.

Examples of additional host or receiving compounds include emitting compounds and/or host compounds of the type shown and described in Applicants' co-pending U.S. Patent Application Serial No. 08/693,359, filed 6 August 1996. Further representative examples of the present invention include emitting compounds according to Formula XII:

10

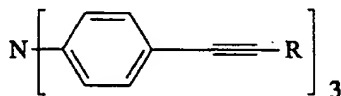
(XII)



wherein M is a trivalent metal ion of a metal such as Al or Ga; and R is alkyl, phenyl, substituted alkyl, substituted phenyl, trimethylsilyl, or substituted trimethylsilyl; and wherein X, Y, and Z are each individually and independently C or N, such that at least two of X, Y and Z are N; and of Formula XIII:

20

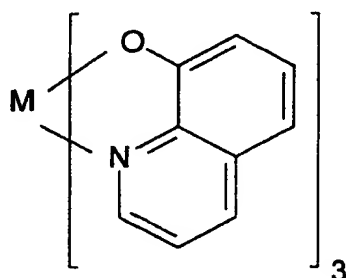
(XIII)



Specific examples of compounds according to Formula I are provided in Fig. 20, which are all commercially available species (Aldrich Chemical Co., Inc.).

- 5 A frequently used emitting compound utilized in those green-emitting OLED's, as disclosed in a number of United States Patents assigned to Kodak (see, for example U.S. Patent No. 5,552,678 to Tang et al.), is a quinolate complex of the general formula:

10



- wherein M is a trivalent ion of metals such as aluminum and gallium. An exemplary green-emitting compound according to this general formula would be tris(8-hydroxyquinolato)
- 15 aluminum, also referred to as Alq₃. Compounds of the present invention as represented by formulas XII and XIII have a red-shifted emission due to the altered ligand structure. The selection of the compounds of formula XII is based on the observation that the incorporation of two nitrogen heteroatoms
- 20 into the pyridil side of the quinolate ligand results in a shift of emission wavelength of 100 nm relative to the emission from Alq₃.

- Using this approach for red-shifting the emission of an OLED,
- 25 the compounds of Formulas XII have been devised and synthesized with the specific purpose of shifting the emission from Alq₃-type receiving compound materials toward shorter

wavelengths. The ligand of Formula XII is an example of a fused ring, multi-heteroatom structure that offers many of the same structural features of the quinolate-based ligands, yet has an emission shifted considerably from that of Alq₃.

5

The compound represented by Formula XIII, although not a metal complex, may be prepared as the hole conducting material for an HTL layer in an OLED. In addition to functioning as the hole transporting material the compound of formula XIII also exhibits satisfactory emissive characteristics as well. The emissive properties of this compound, as well as a compound of Formula XII, are summarized below. Also provided are comparable data for the Alq₃ compound.

15

TABLE 1		
Compound	absorption λ	emission λ
Alq ₃	380 nm	540 nm
XII	280 nm	390 nm
XIII	355 nm	402 nm

20

In accordance with another embodiment of the present invention, Fig. 22 shows a high contrast TOLED display under bright ambient light conditions, such as in sunlight. The high contrast TOLED display of the present invention comprises a TOLED display TD and a low-reflectance absorber, such as a black absorber BA arranged behind the display TD. The TOLED display TD can be fabricated as disclosed in U.S. Patent Applications Serial Nos. 08/354,674 and 08/613,207, incorporated herein by reference in their entirety.

30

As illustrated in Fig. 22, light R emitted from a bright light source L, such as the sun, passes through the various layers of the TOLED display TD and is absorbed by the black absorber BA. As a result, light I emitted by the display TD and viewed by a viewer V is not washed out by ambient light which is

35

reflected by the display, as is the case with conventional displays.

A cross-sectional view of an embodiment of a high contrast display in accordance with the present invention is shown in Fig. 23. A TOLED 1 is arranged over a transparent substrate 2 which is arranged over a low-reflectance absorber 3. Light I emitted from the TOLED 1 propagates toward the viewer. The TOLED 1, which is comprised of several different layers of materials is shown, for simplicity, as one layer. The transparent substrate 2 can be comprised of glass or of plastic, which may be flexible or rigid.

The low-reflectance absorber 3 can be comprised, for example, of a layer of paper or cardboard painted or printed black at least on the side facing the substrate 2. The low-reflectance absorber 3 can also be deposited directly onto the bottom side of the substrate 2, such as by painting the bottom of the substrate with a black, preferably matte, paint. The low-reflectance absorber 3 can also be implemented by spin coating carbon black onto a polymer matrix or by evaporation deposition.

A cross-sectional view of a second embodiment of a high contrast display in accordance with the present invention is shown in Fig. 24. In this embodiment, a low-reflectance absorber 3 is arranged between a TOLED 1 and a substrate 2. In the embodiment of Fig. 24, the low-reflectance absorber 3 is deposited onto the substrate 2. The substrate 2 need not be transparent. The low-reflectance absorber 3 and the substrate 2 can also be implemented as one layer.

Because it is desirable to make the surface of the low-reflectance absorber 3 facing the viewer as absorptive as possible, this surface may be relatively rough and thus may be undesirable for the fabrication thereon of the TOLED 1. As such, if need be, a planarizing layer 4 can be deposited on

the reflectance absorber 3 to provide a smooth surface on which to deposit the TOLED 1. The planarizing layer 4 can be comprised, for instance, of a polymer or plastic and can be applied by spin coating.

5

While the low-reflectance absorber can be implemented, as described above, as a "black absorber," the present invention may also embrace the use of a low-reflectance absorber having a color different from that of the color emitted by the TOLED.

10 For example, a dark green absorber behind a red-emitting TOLED, or still other combinations of selected colors, may also be used within the scope of the subject invention so as to provide a high color contrast display. The low-reflectance surface, thus, may have a high light absorption across the
15 entire visible region of the spectrum so as to produce a gray-to-black surface or it may have high absorption only over that part of the spectral region corresponding to the wavelength region generated by the light emitting device. Preferably, the absorption of light is at least about 50%, and more
20 preferably, about 80-90%, or still higher, for a black absorber.

In order to extract even more EL light in the direction normal to the OLED, an antireflection (AR) coating can be deposited
25 on the transparent ITO anode. For a conventional OLED, this entails depositing the AR coating on top of the transparent substrate prior to the deposition of the ITO layer and the rest of the OLED layers. In such a configuration, care must be taken to account for the reflections in the transparent
30 substrate. For an IOLED, the EL light does not travel through the substrate, simplifying the AR coating design. Also, with the IOLED, the AR coating can be deposited directly on the anode and thus can at the same time serve as a passivating layer for protecting the IOLED from atmosphere-related
35 degradation.

The IOLED structure of the present invention can also be fabricated with one or more filter structures for controlling the spectral width of the light emitted. Fig. 29 shows an IOLED 50 fabricated over a distributed Bragg reflector (DBR) structure 60 which is fabricated on a substrate 70. A DBR structure may also be referred to as a multilayer stack (MLS), such as taught by H. A. MacLeod, Thin Film Optical Filters 94-110 (1969). The DBR structure 60 is formed as a 1/4-wavelength stack 62 of highly reflective layers of dielectric material. The stack 62 can be formed with two to ten alternating layers of titanium oxide TiO_2 and silicon oxide SiO_2 . A layer 61 of ITO is deposited on the stack 62. The cathode 55 of the OLED 50, which is formed as a thin, semi-transparent layer of Mg:Ag alloy, is deposited on the ITO layer 61. The ETL/EL layer 54, HTL 53, protection layer 52 and ITO anode 51 are then deposited in sequence.

The combination of the ITO anode 51 and the bottom DBR structure 60 can provide good cavity and microcavity effect. In particular, if the thickness of the ETL/EL layer 54 is substantially equal to $\lambda/2n$, where λ is the wavelength of the emitted light and n is the refractive index of the ITO anode layer 51 (which is approximately 2.0, relative to air), spectral narrowing is achieved with a considerable increase in the effective efficiency of the OLED.

To narrow the spectrum of the light emitted by the OLED of Fig. 29 even further, another DBR structure can be placed on top of the OLED 50. This, however, requires that electrical access to the anode 51 of the OLED be provided from a side of the combined structure. As an alternative, such a top-side DBR can be replaced by a color filter layer consisting of, for example, an organic dye film.

The present invention further provides monochromatic and multicolor light emitting devices that make use of phosphor layers to downconvert the color of light emitted from organic

light emitting materials into different colors. In one embodiment of the invention, a downconversion layer is used to convert blue light emitted from an organic light emitting layer into red light within a stacked arrangement of OLEDs.

5 In another embodiment of the invention, downconversion layers are used to convert blue light emitted from organic light emitting layers into green and/or red light. The light emitting devices of the present invention are used in a variety of monochromatic and multicolor applications to
10 provide displays with high brightnesses and efficiencies.

The present invention may also provide organic light emitting devices which make use of downconversion phosphor layers to provide displays of high efficiency and brightness. A light
15 emitting device in accordance with the present invention comprises a plurality of organic light emitting layers in a stacked arrangement and a downconversion phosphor layer disposed between any two of the plurality of organic light emitting layers.

20 In a first embodiment of the present invention that relates to downconversion phosphors, a light emitting device 100 is provided as shown in Fig. 25. In this stacked arrangement of organic light emitting layers, a first blue light emitting
25 layer 112 is provided over substrate 111, green light emitting layer 113 is provided over first blue light emitting layer 112, red downconversion phosphor layer 114 is provided over green light emitting layer 113, and second blue light emitting layer 115 is provided over downconversion phosphor layer 114.
30 Disposed between the light emitting layers are transparent, conductive layers 120, 121, 122 and 123. Metal contact layer 130 is provided over second blue light emitting layer 115.

Disposed between green light emitting layer 113 and red
35 downconversion phosphor layer 114 is a mirror structure 125, which is preferably a multilayer stack of dielectric material. Mirror structure 125 shown in Fig. 25 is characterized by a

red pass-band and blue and green blocking bands to prevent the pumping of red downconversion phosphor layer 114 by green and blue light emitting layers, 113 and 112, respectively. By reflecting green and blue light, mirror structure 125 also
5 serves to increase device efficiency by a factor of at least two. Moreover, mirror structure 125 results in the efficient pumping of red downconversion phosphor layer 114 by second blue light emitting layer 115 such that layer 114 is much less thick than is necessary for a single-pass device. For
10 example, red downconversion phosphor layer 114 is as thin as 1000 Å.

Mirror structure 125 is any suitable material to permit the passage of red light but block the passage of green and blue
15 light, as is known in the art. For example, mirror structure 125 comprises at least two dielectric materials with different dielectric constants arranged in a multilayer stack. The thickness of the layers in the stack define the range of wavelengths that are permitted to pass through the structure.
20 Typical inorganic dielectric materials to form mirror structure 125 include $\text{SiO}_2/\text{TiO}_2$ and $\text{SiO}_2/\text{SiN}_x$. Although such inorganic materials are within the scope of the present invention, the use of organic dielectric materials such as 3, 5, 7, 8 naphthalene tetracarboxylic dianhydride ("NTCDA") and
25 polytetrafluorethylene (TEFLON) are preferred. The use of organic dielectric materials minimizes the risk of damaging the organic light emitting materials during deposition of the dielectric materials used for mirror structure 125.

30 As is known in the art, light emitting layers 112, 113 and 115 are made from organic materials that emit light when excited by electric current. Therefore, the light emitting device shown in Fig. 25 will emit blue light when a voltage is applied across conductive layers 120 and 121, and green light
35 when voltage is applied between conductive layers 121 and 122. To emit red light, a voltage is applied between conductive layer 123 and metal contact layer 130 so that second blue

light emitting layer 115 emits blue light, which is then converted to red light by red downconversion phosphor layer 114. Blue light emitted from second blue light emitting layer 115 is not permitted to pass through mirror structure 125 and therefore resonates between layers 125 and 130, thereby causing the efficient pumping of red downconversion phosphor layer 114. The resulting emission of red light passes through light emitting layers 113 and 112 and into substrate 111. The configuration shown in Fig. 25 permits the more efficient emission of red light than is possible with the use of red organic light emitting layers.

In the embodiment shown in Fig. 25, substrate 111 is a substantially transparent material, such as glass, quartz, sapphire or plastic. For simplicity, the light emitting layers 112, 113 and 115 are shown as single layers in the drawing. As is well-known in the art, however, these layers actually comprise multiple sublayers (e.g., HTL's, EL's and ETL's) when they are not single-layer polymer devices. The arrangement of the sublayers obviously depends on whether the device is of DH (double heterostructure) or SH (single heterostructure) configuration.

Where a transparent, conductive layer serves as both cathode for one light emitting layer and anode for another, such as layer 121, it preferably comprises indium-tin-oxide ("ITO"). Where a transparent, conductive layer does not serve as both cathode and anode, such as layer 122, which serves as cathode for green light emitting layer 113 but is separated from second blue light emitting layer 115 by mirror structure 125, it preferably comprises a compound electrode such as a semi-transparent low work function metal and ITO. An anode layer that does not serve as both cathode and anode, however, is nonetheless preferably ITO. Metal contact layer 130 comprises any suitable material, such as magnesium, lithium, aluminum, silver, gold and alloys thereof.

In another embodiment of the invention, green downconversion phosphor layer 126 is inserted between red downconversion phosphor layer 114 and second blue light emitting layer 115, as shown in Fig. 26. Layer 126 results in the more efficient
5 conversion of blue to red light by the intermediate conversion of blue to green light.

In another embodiment of the invention, blue light emitting layers are used to pump both red and green downconversion
10 phosphor layers, as shown in Fig. 27. In device 200, a first blue light emitting layer 112 is provided over substrate 111, green downconversion phosphor layer 126 is provided over first blue light emitting layer 112, second blue light emitting
15 layer 115 is provided over green downconversion layer 126, red downconversion phosphor layer 114 is provided over second blue light emitting layer 115, and third blue light emitting layer 127 is provided over red downconversion phosphor layer 114. Disposed between the light emitting layers are transparent,
20 conductive layers 120, 121, 122, 123 and 125. Metal contact layer 130 is provided over third blue light emitting layer 127. In addition, first and second mirror structures 128 and 125, respectively, are disposed between first blue light emitting layer 112 and green downconversion layer 126, and
25 between second blue light emitting layer 115 and red downconversion phosphor layer 114, respectively. First mirror structure 128 permits the passage of red and green light while blocking the passage of blue light. Second mirror structure 125 permits the passage of red light while blocking the
30 passage of green and blue light.

As representative embodiments of the subject invention in which the OLED further includes a downconversion phosphor layer, such an OLED may be comprised of: a transparent
35 substrate; a first blue organic light emitting layer over said substrate; a green organic light emitting layer over said first blue organic light emitting layer; a mirror structure over said green organic light emitting layer, said mirror

structure comprising a multilayer stack of at least one dielectric material, said mirror structure allowing the passage of red light and blocking the passage of blue and green light; a red downconversion phosphor layer over said mirror structure; and a second blue organic light emitting layer over said red downconversion phosphor layer.

Such an OLED containing a downconversion phosphor layer may, alternatively, be comprised of: a transparent substrate; a first blue organic light emitting layer over said substrate; a first mirror structure over said first blue organic light emitting layer, said mirror structure comprising a multilayer stack of at least one dielectric material, said mirror structure allowing the passage of red and green light and blocking the passage of blue light; a green downconversion phosphor layer over said first mirror structure; a second blue organic light emitting layer over said green downconversion phosphor layer; a mirror structure over said second blue organic light emitting layer, said mirror structure comprising a multilayer stack of at least one dielectric material, said mirror structure allowing the passage of red light and blocking the passage of blue and green light; a red downconversion phosphor layer over said mirror structure; and a third blue organic light emitting layer over said red downconversion phosphor layer.

The light emitting devices of the present invention optionally comprises a layer 140 of low-loss, high refractive index dielectric material, such as titanium dioxide (TiO_2), between transparent conductive layer 120 and substrate 111. Layer 140 is especially preferred when transparent, conductive layer 120 is made from ITO, which is a high-loss material. The refractive indexes for TiO_2 and ITO are approximately 2.6 and 2.2, respectively. Layer 140 therefore substantially eliminates waveguiding and absorption in the ITO, the light emitted from light emitting layers 112, 113 and 115 now being easily transmitted through layer 140 and substrate 111.

This invention will now be described in detail with respect to showing how certain specific representative embodiments thereof will be made, the materials, apparatus and process steps being understood as examples that are intended to be
5 illustrative only. In particular, the invention is not intended to be limited to the methods, materials, conditions, process parameters, apparatus and the like specifically recited herein.

10

EXAMPLES

Prior to deposition of the organic films for the representative OLEDs of the present invention, (100) Si substrates may be cleaned by sequential ultrasonic rinses in detergent solution and deionized water, then boiled in 1,1,1-
15 trichloroethane, rinsed in acetone, and finally boiled in 2-propanol. Between each cleaning step, the substrates may be dried in high purity nitrogen. The background pressure prior to deposition is normally 7×10^{-7} torr or lower and the pressure during the deposition is about 5×10^{-7} to 1.1×10^{-6}
20 torr.

I. IOLED with a protection layer

An IOLED structure (Fig. 1) was grown starting with the thermal evaporation in vacuum of a 1000 Å thick cathode
25 consisting of 25:1 Mg-Ag alloy, followed by a 500 Å thick aluminum tris(8-hydroxyquinoline) (Alq_3) electron transporting and electroluminescent (EL) layer, and a 250 Å thick hole transporting layer (HTL) of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD).
30 Alternatively, IOLEDs employing 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (α -NPD) as the HTL were also fabricated, with results similar to those obtained using TPD. To protect the fragile HTL from the sputter deposition of the top ITO anode contact, either a 3,4,9,10-perylenetetracarboxylic
35 dianhydride (PTCDA) or a copper phthalocyanine (CuPc) film was employed.

Typical organic deposition rates ranged from 1 Å/s to 5 Å/s with the substrate held at room temperature. Finally, the top ITO layer was deposited by RF magnetron sputtering of a pressed ITO target in a 2000:1 Ar:O₂ atmosphere, and 5 mTorr pressure. The RF power was 5W, which resulted in a deposition rate of 200 Å/hour.

The forward bias current-voltage (I-V) characteristics of 0.05 mm² IOLEDs with PTCDA and CuPc PCLs, as well as of a device with no PCL are shown in Fig. 2. Fig. 3 shows the light intensity vs. current (L-I) response of the IOLEDs in Fig. 2.

An OLED was also prepared comprised of structure having the following sequence of layers: an ITO layer/60Å PTCDA/500Å NPd/500Å Alq₃/1000Å MgAg/500Å Ag and a similar OLED, but without the PTCDA layer. The current vs. voltage of this device is shown in Fig. 5.

II. OLEDs fabricated with improved ITO deposition method

In a representative example of the present invention in which the improved ITO deposition method was used, a commercially available glass substrate precoated with ITO, from Southwall Technologies, Inc., Palo Alto, California, USA, was used. A hole transport layer comprised of about 300 Å of TPD was deposited onto the ITO anode layer, an electron transporting layer comprised of about 500 Å of tris-(8-hydroxyquinoline) aluminum(Alq₃) was deposited onto the TPD hole transporting layer and a cathode layer of about 120 Å Mg-Ag was deposited onto the Alq₃ electron transporting layer.

An ITO layer according to the present invention was then prepared by depositing about 150 Å of ITO using only 5W of RF power in the presence of about 200 sccm Ar and 0.1 sccm O₂ onto the Mg-Ag cathode layer and then an additional 400 Å of ITO was deposited using 45W RF power in the presence of about 200 sccm Ar and about 0.42 sccm O₂.

Fig. 7 shows the current-voltage (I-V) characteristics of this heterostructure. There was no practically discernible difference between the I-V characteristics of this device as compared with an OLED having the entire ITO layer deposited at the slower deposition rate.

Although the particular OLED structure of Fig. 6 has been described, it is to be understood that any OLED structure having an ITO layer deposited using a low initial deposition rate and then a substantially higher deposition rate would be in accordance with this invention.

III. OLEDs with an electron transporting layer containing an organic free radical

1. A single heterostructure containing an organic free radical.

A transparent substrate, is pre-coated with an indium tin oxide (ITO) layer having a sheet resistance of about 15 Ω /square. The substrate may be ultrasonically cleaned in detergent, followed by thorough rinsing in deionized water, 1,1,1-trichloroethane, acetone and methanol, and dried in pure nitrogen gas between each step. The clean dry substrate is then transferred to the vacuum deposition system. All organic and metal depositions may then be carried out under high vacuum ($< 2 \times 10^{-6}$ Torr). Depositions are carried out by thermal evaporation from baffled Ta crucibles at a nominal deposition rate of 2-4 \AA /s. First, an approximately 350 \AA layer of N,N'-diphenyl-N,N'-bis(3-methyphenyl)-1,1-biphenyl-4,4'-diamine (TPD) may be vapor deposited on the cleaned ITO substrate. A sample of $M(C_5Ph_5)_2$, (where M may be Ge or Pb) may then be heated to ca. 250°C, liberating Cp^\bullet , which may be deposited as a layer on top of the TPD film. The final thickness of the Cp^\bullet film may be about 400 \AA . An array of circular 250 mm diameter 1,000 \AA electrodes of approximately 10:1 Mg:Ag atomic ratio may be subsequently deposited by co-evaporation from separate Ta boats. A 500 \AA thick layer of Ag may be deposited to inhibit atmospheric oxidation of the electrode.

2. A double heterostructure containing an organic free radical

A double heterostructure may be fabricated by including a
5 separate emissive layer, which may be formed as doped or un-
doped tris-(8-hydroxyquinoline) aluminum Alq_3 . The double
heterostructure may be prepared substantially as described for
the single heterostructure structure, except that after
depositing the TPD layer and before depositing the organic
10 free radical layer, a separate emissive layer of Alq_3 is
deposited.

IV. OLEDs with alternative host and/or dopant materials

In these particular embodiments, in which the alternative host
15 and/or dopant materials of the present invention were prepared
and incorporated into an OLED, the hole transport layer was
comprised of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1-1'-biphenyl-
4,4'-diamine (TPD), and the electron transporting layer was
comprised of the doped or undoped tris-(5-hydroxyquinoxaline)
20 aluminum (Alx_3) or of doped or undoped Alq_3 .

The hole transporting material TPD and the electron
transporting materials Alq_3 and Alx_3 were synthesized according
to literature procedures, and were sublimed before use.
25

The dopant C_{60} was purchased from Southern Chemical Group, LLC,
and used as received.

The bisphenol-squarilium dopant of formula XI and the indigo
30 dye compound dopant were purchased from Aldrich Chemical Co.,
Inc., and sublimed twice to give the pure green and purple
crystalline materials, respectively.

Aluminum tris(5-hydroxyquinoxaline), (Alx_3), was prepared by
35 the reaction of aluminum trisisopropoxide with 5-
hydroxyquinoxaline in isopropanol under argon. Isopropanol

was dried over CaH_2 before use. The amount of the ligand taken for the reaction was in slight excess. The isopropanol mixture was refluxed under argon for one and a half hours, and orange product was isolated by rotarvaporization.

5

Gallium tris(5-hydroxyquinoxaline), (GaX_3) , was formed by mixing 200 ml water solution of $0.2\text{g Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ and an excess of 1% alcoholic solution of the ligand at 60°C , followed by 10% ammonium hydroxide addition to make the solution slightly basic. Orange precipitate was obtained, and, after cooling, filtered off. The GaX_3 preparation was similar to that described in *Spectrochimica Acta*, 1956, Vol. 8, pp.1-8.

For the reagents, 5-hydroxyquinoxaline was prepared according to S.K. Freeman, P.E. Spoerri, *J. Org. Chem.*, 1951, 16, 438; aluminum trisisopropoxide (99.99% purity) and $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (99.999% purity) were bought from Aldrich Chemical Co.; and isopropanol was obtained from Fisher Scientific.

The ITO/Borosilicate substrates ($100\Omega/\text{square}$) were prepared using standard procedures. All the chemicals were resistively heated in various tantalum boats. TPD was first deposited at a rate from one to four $\text{\AA}/\text{s}$. The thickness was typically controlled at about 300 \AA .

25

The electron transporting layer (Alq_3 , Alx_3) was doped with various dyes (C_{60} , the bisphenol squarilium dye and the indigo dye compound of formula IX). Typically, the dopant was first vaporized with the substrates covered. After the rate of the dopant was stabilized, the host material was vaporized at the prescribed rate. The cover over the substrates was then opened and the host and guest were deposited at the desired concentration. The rate of dopant was normally 0.1 - 0.2 $\text{\AA}/\text{s}$. The total thickness of this layer was controlled at about 450 \AA .

35

The substrates were then released to air and masks were put directly on the substrates. The masks are made of stainless steel sheet and contain holes with diameters of 0.25, 0.5, 0.75, and 1.0 mm. The substrates were then put back into
5 vacuum for further coating.

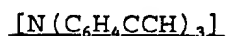
Magnesium and silver were co-deposited at a rate normally of 2.6 Å/s. The ratio of Mg:Ag varied from 7:1 to 12:1. The thickness of this layer was typically about 500 Å. Finally,
10 1000 Å Ag was deposited at the rate between one to four Å/s.

The I-V characteristics of these OLEDs were measured and are shown for the doped and undoped Alx₃ in Fig. 13. The close similarity of the results with and without the dopant shows
15 that the dopant is not perturbing the electrical properties of the device.

For the OLEDs containing an emissive electron transporting layer of Alq₃ (as the host material with and without the same
20 fluorescent dye dopant, wherein the energy match between the host material and the dopant was poor) nearly all of the EL emission was obtained from the Alq₃.

V. Preparation of a Compound of Formula XII wherein M = Ga

25 A 0.25-g sample of 4-hydroxypyrazolo[3,4-d]pyrimidine is dissolved in 2.5 mL of aqueous 1.1 M NaOH. A solution prepared by dissolving 0.114 g of gallium nitrate in 1.5 mL of water is added slowly to the NaOH solution. A precipitate forms upon addition of the gallium nitrate. The white precipitate was
30 isolated by filtration, washed twice with 5-mL aliquots of ethanol, and air dried. The isolated product, when excited at 250 nm, has an emission maximum at 390 nm.

VI. Preparation of Compounds of Formula XIII1. Preparation of tris(4-ethynylphenyl) amine

A solution of aqueous KOH is prepared by dissolving 1.26 g
5 (0.0225 mol) in methanol. The KOH solution is added to a
solution of tris(4-trimethylsilylethynylphenyl)amine that was
prepared by adding 2.00 g (0.0038 mol) to 100 mL of
tetrahydrofuran (THF), creating an orange solution that was
stirred at room temperature for 3 hours. The small amount of
10 orange precipitate that formed was removed by filtering the
reaction mixture through Celite. The Celite was washed with
two 10-mL portions of THF. The solvent was removed from the
combined filtrates *in vacuo* leaving a gummy beige-orange
residue. The residue was triturated with 50 mL of methanol and
15 left to stir for one hour at room temperature.

The product corresponding to Formula XIII was obtained as an
orange powder that was collected, washed with 2 5-mL portions
of pentane and dried *in vacuo*. Two additional crops were
20 obtained from the filtrates in a similar manner, providing a
total yield of 0.746 g (63%). The emission characteristics of
the compound at an excitation wavelength of 346 nm, were as
follows:

emission (solution):	430 nm
25 emission (solid):	517 nm

2. Preparation of tris(4-trimethylsilylethynyl-phenyl)amine

30 A 100-mL Schenk flask is charged with 1.8 g of
trimethylsilylacetylene, 15 mL of diethylamine, 2.0 g of
tris(4-bromophenyl)amine, 0.59 g of $PdCl_2$, 0.175 g of
triphenylphosphine and 0.032 of copper(II) iodide. The
35 reaction mixture is heated to reflux for 24 hours. The solvent
is removed *in vacuo*, and the residue extracted with 70 mL of
benzene, followed by 70 mL of diethylether. Both organic

extracts are filtered through alumina, combined and the solvent removed *in vacuo*. The resulting solid has a melting point of 155 - 158 °C and shows strong blue fluorescence. Excitation at either 255 or 350 nm gives luminescence centered at 402 nm.

VII. Preparation of an OLED containing an emissive material according to Formula I

A transparent substrate (e.g. glass or plastic) is precoated with an indium tin oxide (ITO) layer having a sheet resistance of about 15 Ω /square. The substrate may be cleaned by thorough rinsing in deionized water, 1,1,1-trichloroethane, acetone and methanol, and dried in pure nitrogen gas between each step. The clean, dry substrate is then transferred to the vacuum deposition system. All organic and metal depositions may then be carried out under high vacuum ($< 2 \times 10^{-6}$ torr). Depositions are carried out by thermal evaporation from baffled Ta crucibles at a nominal deposition rate of 2-4 angstroms/second. First, an approximately 350 Å layer of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,11-biphenyl-4,41-diamine (TPD) may be vapor deposited onto the cleaned ITO substrate. A sample of a compound according to Formula XII and a selected fluorescent dye are then heated in separate Ta boats to deposit a film on top of the TPD film that is a mixture of 0.1-10 mole % dye in the receiving compound according to Formula XII. The emission color of the OLED will be dictated by the luminescent properties of the dye itself, and can span the entire visible spectrum by appropriate choice of the dye. This mixed film according to the present invention is deposited to a thickness of about 400 Å. An array of circular, 0.25-mm diameter, 1000-Å electrodes of approximately 10:1 Mg:Ag ratio may be subsequently deposited by co-evaporation from separate Ta boats. A 500 Å-thick layer of Ag may then be added to inhibit atmospheric oxidation of the electrode.

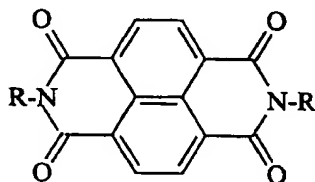
VIII. Preparation of an OLEDs containing an emissive material according to Formula XIII

A transparent substrate (e.g. glass or plastic) is precoated with an indium tin oxide (ITO) layer having a sheet resistance of about 15 ohm/square. The substrate may be cleaned by thorough rinsing in deionized water, 1,1,1-trichloroethane, acetone and methanol, and dried in pure nitrogen gas between each step. The clean, dry substrate is then transferred to the vacuum deposition system. All organic and metal depositions may then be carried out under high vacuum ($< 2 \times 10^{-6}$ torr). Depositions are carried out by thermal evaporation from baffled Ta crucibles at a nominal deposition rate of 2-4 angstroms/second. First, a sample of a compound according to Formula XIII and a selected fluorescent dye are heated in separate Ta boats to deposit a film on the cleaned substrate that is a mixture of 0.1-10 mole % dye in compound II. The emission color of the OLED will be dictated by the luminescent properties of the dye itself, and can span the entire visible spectrum by appropriate choice of the dye. This mixed film according to the present invention is deposited to a thickness of about 400 angstroms. Next a film of a suitable hole blocking material is deposited, such as 100 Å of an oxadiazole derivative (e.g. 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole), followed by film of an electron transporting material (ca. 300 Å) such as aluminumtris(8-hydroxyquinoline). An array of circular, 0.25-mm diameter, 1000-Å electrodes of approximately 10:1 Mg:Ag ratio may be subsequently deposited by co-evaporation from separate Ta boats. A 500 Å thick layer of Ag may then be added to inhibit atmospheric oxidation of the electrode.

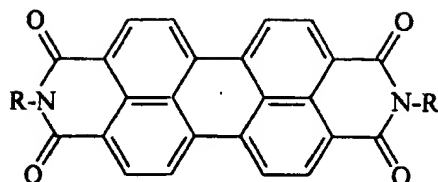
Those of skill in the art may recognize certain modifications to the various embodiments of the invention, which modifications are meant to be covered by the spirit and scope of the appended claims.

What Is Claimed Is:

1. An organic light emitting device comprising an electroluminescent layer between a pair of electrodes wherein a protection layer is present between said electroluminescent layer and at least one of said electrodes.
2. The organic light emitting device of claim 1 wherein said electroluminescent layer is contained in a heterostructure for producing electroluminescence with said protection layer being between a hole transporting layer and an anode layer.
3. The organic light emitting device of claim 2 wherein said heterostructure is a single heterostructure.
4. The organic light emitting device of claim 2 wherein said heterostructure is a double heterostructure.
5. The organic light emitting device of claim 1 wherein said protection layer is comprised of a perylene, naphthalene, isoquinoline, phthalocyanine or phenanthroline based compound.
6. The organic light emitting device of claim 5 wherein said compound is 3,4,9,10-perylenetetracarboxylic dianhydride; a phthalocyanine compound; 3,4,7,8-naphthalenetetracarboxylic dianhydride; 3,4,9,10-perylenetetracarboxylic dianhydride; bis(1,2,5-thiadiazolo)-p-quinobis(1,3-dithiole); 1,4,5,8-naphthalenetetracarboxylic dianhydride;



where R = H, alkyl or aryl;



where R = H, alkyl or aryl;

a compound having the CA index name, bisbenzimidazo[2,1-a:1',2'-b']anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-10,21-dione;

a compound having the CA index name, bisnaphth[2',3':4,5]imidazo[2,1-a:2',1'-a']anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-10,21-dione;

a compound having the CA index name, bisbenzimidazo[2,1-b:2',1'-i]benzo[lmn][3,8]phenanthroline-8,1-dione;

a compound having the CA index name, benzo[lmn]bisnaphth[2',3':4,5]imidazo[2,1-b:2'1'-I][3,8]phenanthroline-9,20-dione;

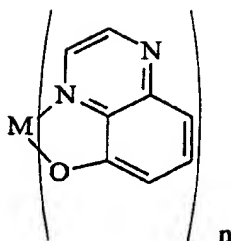
or a substituted derivative of one of said compounds.

7. The organic light emitting device of claim 6 wherein said protection layer comprises said 3,4,9,10-perylenetetra-carboxylic dianhydride.

8. The organic light emitting device of claim 5 wherein said protection layer comprises copper phthalocyanine.

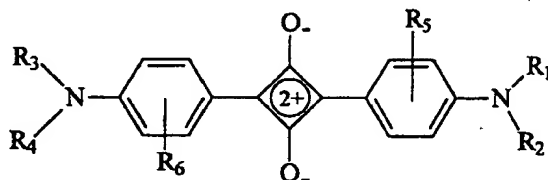
9. The organic light emitting device of claim 2 wherein said heterostructure contains an electron transporting layer comprised of an organic free radical.

10. The organic light emitting device of claim 2 wherein said heterostructure for producing electroluminescence contains an emissive layer comprised of a host material and a dopant, said host material being comprised of a metal complex of (5-hydroxy)quinoxaline having the chemical structure of formula:



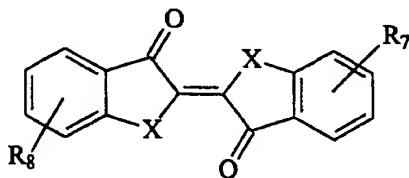
wherein if M is Al, Ga or In, then $n = 3$, and if M is Zn or Mg, then $n = 2$.

11. The organic light emitting device of claim 10 wherein said dopant is comprised of a bisphenyl-squarilium compound of formula:



wherein R_1 , R_2 , R_3 and R_4 are, independently of each other, an unsubstituted or substituted alkyl, aryl or heterocycle, and R_5 and R_6 are, independently of each other, an unsubstituted or substituted alkyl, aryl, OH or NH_2 .

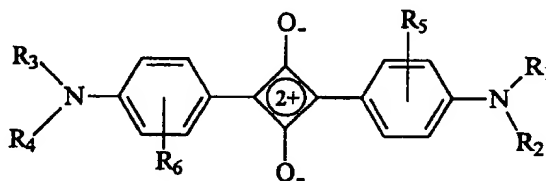
12. The organic light emitting device of claim 10 wherein said dopant comprises an indigo dye compound having a chemical structure of formula:



wherein X = NH, NR₉, S, Se, Te, or O, wherein R₉ is alkyl or phenyl, and R₇ and R₈ are, independently of each other, an unsubstituted or substituted alkyl or aryl group, a π -electron donor group or a π -electron acceptor group.

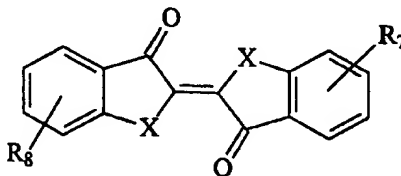
13. The organic light emitting device of claim 10 wherein said dopant comprises a fullerene compound.

14. The organic light emitting device of claim 2 wherein said heterostructure contains an emissive layer comprised of a host material and a dopant, said dopant being comprised of a compound of formula:



wherein R₁, R₂, R₃ and R₄ are, independently of each other, an unsubstituted or substituted alkyl, aryl or heterocycle, and R₅ and R₆ are, independently of each other, an unsubstituted or substituted alkyl, aryl, OH or NH₂.

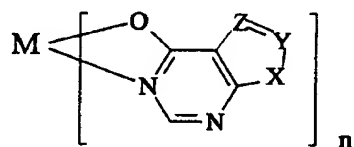
15. The organic light emitting device of claim 2 wherein said heterostructure contains an emissive layer comprised of a host material and a dopant, said dopant being comprised of an indigo dye compound of formula:



wherein X = NH, NR₉, S, Se, Te, or O, wherein R₉ is alkyl or phenyl, and R₇ and R₈ are, independently of each other, an unsubstituted or substituted alkyl or aryl group, a π -electron donor group or a π -electron acceptor group.

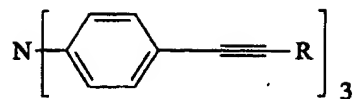
16. The organic light emitting device of claim 2 wherein said heterostructure contains an emissive layer comprised of a host material and a dopant, said dopant being comprised of a fullerene compound.

17. The organic light emitting device of claim 2 wherein said heterostructure contains an emissive layer comprised of a host compound represented by formula:



wherein M is an ion of a divalent or trivalent metal atom, wherein when M is trivalent, $n = 3$, and when M is divalent, then $n = 2$, wherein the metal atom is selected from the group consisting of aluminum, gallium, indium, and zinc, and wherein X, Y, and Z are each individually and independently C or N, such that at least two of X, Y and Z are N.

18. The organic light emitting device of claim 2 wherein said heterostructure contains an emissive layer comprised of a host compound having a structure represented by Formula:



wherein R is alkyl, phenyl, substituted alkyl, substituted phenyl, trimethylsilyl, or substituted trimethylsilyl.

19. The organic light emitting device of claim 1 wherein said organic light emitting device is included as one of a plurality of organic light emitting layers in a stacked arrangement; and a downconversion phosphor layer is disposed between any two of said plurality of organic light emitting layers.

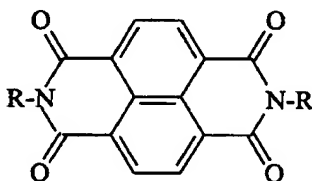
20. The organic light emitting device of claim 1 wherein said organic light emitting device is substantially transparent and a low-reflectance absorber is arranged proximate to the substantially transparent organic light emitting device so as to form a high contrast light emitting display.

21. The use of the organic light emitting device of claim 1 in a panel display, vehicle, computer, television, printer, wall screen, theater screen, stadium, electronic device, lighting device, laser, screen billboard or sign.

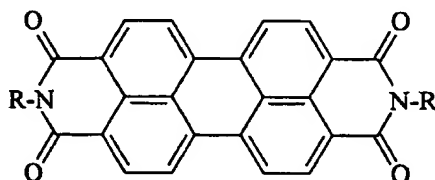
22. An organic light emitting device comprising, in sequence,
a substrate;
a cathode layer;
an electron transporting layer;
a hole transporting layer;
a protection layer; and
an anode.

23. The organic light emitting device of claim 22 wherein said protection layer is comprised of a perylene, naphthalene, isoquinoline, phthalocyanine or phenanthroline based compound.

24. The organic light emitting device of claim 23 wherein said compound is 3,4,9,10-perylenetetracarboxylic dianhydride; 3,4,7,8-naphthalenetetracarboxylic dianhydride; 3,4,9,10-perylenetetracarboxylic dianhydride; bis(1,2,5-thiadiazolo)-p-quinobis(1,3-dithiole); 1,4,5,8-naphthalenetetracarboxylic dianhydride;



where R = H, alkyl or aryl;



where R = H, alkyl or aryl;

a compound having the CA index name, bisbenzimidazo[2,1-a:1',2'-b']anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-10,21-dione;

a compound having the CA index name, bisnaphth[2',3':4,5]imidazo[2,1-a:2',1'-a']anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-10,21-dione;

a compound having the CA index name, bisbenzimidazo[2,1-b:2',1'-i]benzo[lmn][3,8]phenanthroline-8,1-dione;

a compound having the CA index name,
benzo[1mn]bisnaphth[2',3':4,5]imidazo[2,1-b:2'1'-
I][3,8]phenanthroline-9,20-dione;
or a substituted derivative of one of said compounds.

25. The organic light emitting device of claim 24 wherein said protection layer comprises said 3,4,9,10-perylenetetracarboxylic dianhydride.

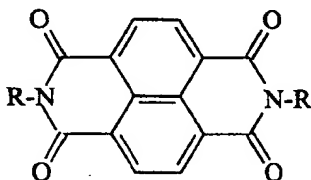
26. The organic light emitting device of claim 23 wherein said protection layer comprises copper phthalocyanine.

27. A method of fabricating an organic light emitting device for producing electroluminescence comprising:

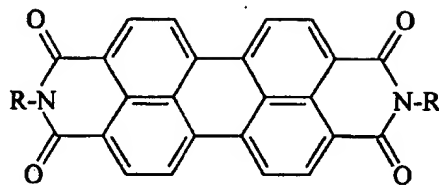
fabricating a heterostructure for producing electroluminescence, wherein the fabrication process includes the step of depositing a protection layer on a hole transporting layer and then depositing an indium tin oxide anode layer on said protection layer.

28. The method according to claim 27 wherein said protection layer is comprised of a perylene, naphthalene, isoquinoline, phthalocyanine or phenanthroline based compound.

29. The organic light emitting device of claim 28 wherein said compound is 3,4,9,10-perylenetetracarboxylic dianhydride; 3,4,7,8-naphthalenetetracarboxylic dianhydride; 3,4,9,10-perylenetetracarboxylic dianhydride; bis(1,2,5-thiadiazolo)-p-quinobis(1,3-dithiole); 1,4,5,8-naphthalenetetracarboxylic dianhydride;



where R = H, alkyl or aryl;



where R = H, alkyl or aryl;

a compound having the CA index name, bisbenzimidazo[2,1-a:1',2'-b']anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-10,21-dione;

a compound having the CA index name, bisnaphth[2',3':4,5]imidazo[2,1-a:2',1'-a']anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-10,21-dione;

a compound having the CA index name, bisbenzimidazo[2,1-b:2',1'-i]benzo[lmn][3,8]phenanthroline-8,1-dione;

a compound having the CA index name, benzo[lmn]bisnaphth[2',3':4,5]imidazo[2,1-b:2'1'-l][3,8]phenanthroline-9,20-dione;

or a substituted derivative of one of said compounds.

30. The method according to claim 29 wherein said protection layer is comprised of said 3,4,9,10-perylenetetracarboxylic dianhydride.

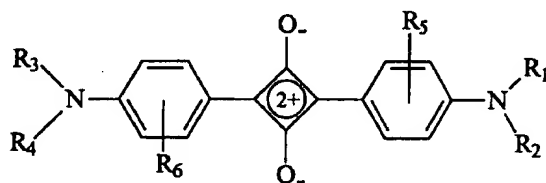
31. The method according to claim 28 wherein said protection layer comprises copper phthalocyanine.

32. The method according to claim 27 wherein the fabrication process includes the steps of:

- (a) depositing indium tin oxide at a low deposition rate to form a protective indium tin oxide layer; and then
- (b) depositing indium tin oxide at a substantially higher deposition rate.

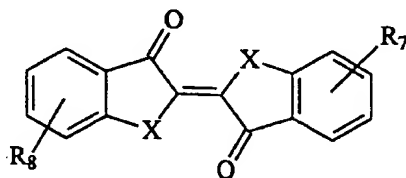
33. The method according to claim 27 wherein the fabrication process includes the step of heating an organometallic complex under vacuum conditions to a temperature sufficient to cause the organometallic complex to form organic free radicals from the gas phase to form an electron transporting layer.

34. The method according to claim 27 wherein the fabrication process includes the step of depositing a layer comprised of a host material and a dopant, said dopant being comprised of a compound of formula:



wherein R_1 , R_2 , R_3 and R_4 are, independently of each other, an unsubstituted or substituted alkyl, aryl or heterocycle, and R_5 and R_6 are, independently of each other, an unsubstituted or substituted alkyl, aryl, OH or NH_2 .

35. The method according to claim 27 wherein the fabrication process includes the step of depositing a layer comprised of a host material and a dopant, said dopant being comprised of an indigo dye compound of formula:



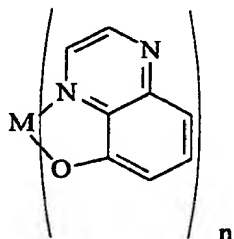
wherein $X = NH$, NR_9 , S , Se , Te , or O , wherein R_9 is alkyl or phenyl, and R_7 and R_8 are, independently of each other, an

unsubstituted or substituted alkyl or aryl group, a π -electron donor group or a π -electron acceptor group.

36. The method according to claim 27 wherein the fabrication process includes the step of depositing a layer comprised of a host material and a dopant, said dopant being comprised of a fullerene compound.

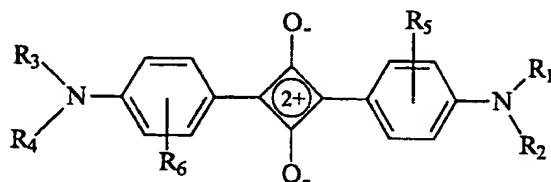
37. An organic light emitting device comprising a heterostructure for producing electroluminescence, wherein said heterostructure contains:

- (1) an electron transporting layer comprised of an organic free radical;
- (2) an emissive layer comprised of a host material and a dopant, said host material being comprised of a metal complex of (5-hydroxy)quinoxaline having the chemical structure of formula:



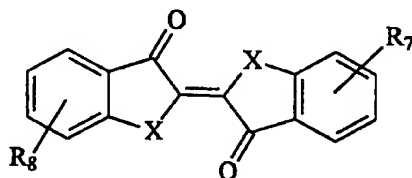
wherein when M is Al, Ga or In, $n = 3$, and when M is Zn or Mg, $n = 2$;

- (3) an emissive layer comprised of a host material and a dopant, said host material being comprised of a compound of formula:



wherein R_1 , R_2 , R_3 and R_4 are, independently of each other, an unsubstituted or substituted alkyl, aryl or heterocycle, and R_5 and R_6 are, independently of each other, an unsubstituted or substituted alkyl, aryl, OH or NH_2 ;

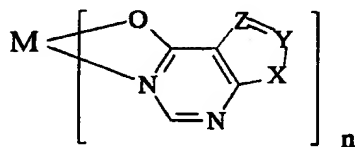
(4) an emissive layer comprised of a host material and a dopant, said dopant being comprised of an indigo dye compound of formula:



wherein $X = NH$, NR_9 , S , Se , Te , or O , wherein R_9 is alkyl or phenyl, and R_7 and R_8 are, independently of each other, an unsubstituted or substituted alkyl or aryl group, a π -electron donor group or a π -electron acceptor group;

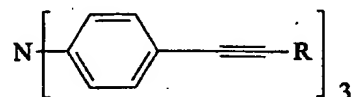
(5) an emissive layer comprised of a host material and a dopant, said dopant being comprised of a fullerene compound;

(6) an emissive layer comprised of a host material and a dopant, said host compound being represented by formula:



wherein M is an ion of a divalent or trivalent metal atom, wherein when M is trivalent, $n = 3$, and when M is divalent, then $n = 2$, wherein the metal atom is selected from the group consisting of aluminum, gallium, indium, and zinc, and wherein X , Y , and Z are each individually and independently C or N , such that at least two of X , Y and Z are N ; or

(7) an emissive layer comprised of a host material and a dopant, said host compound being represented by formula:



wherein R is alkyl, phenyl, substituted alkyl, substituted phenyl, trimethylsilyl, or substituted trimethylsilyl.

38. A high contrast light emitting display comprising:

a substantially transparent organic light emitting device; and

a low-reflectance absorber arranged proximate to the substantially transparent organic light emitting device.

39. A light emitting device comprising:

a substrate;

a plurality of organic light emitting layers in a stacked arrangement over said substrate; and

a downconversion phosphor layer disposed between any two of said plurality of light emitting layers.

40. A light emitting device comprising:

a substrate;

a filter structure over said substrate;

a downconversion phosphor layer over said filter structure; and

an organic light emitting layer over said downconversion phosphor layer.

1/22

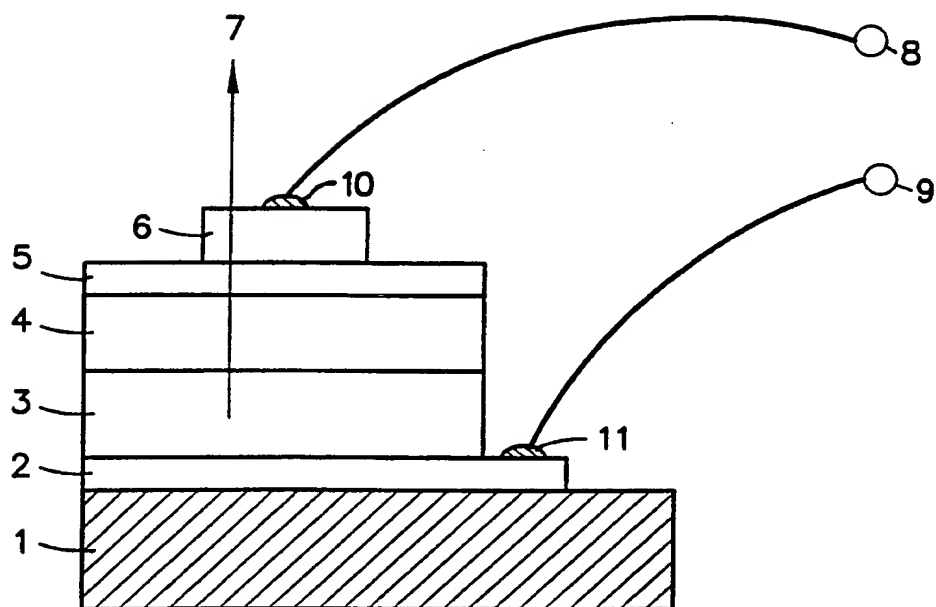


FIG. 1

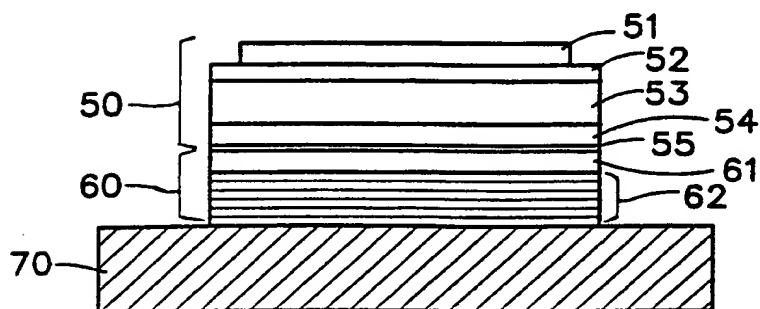


FIG. 29

2/22

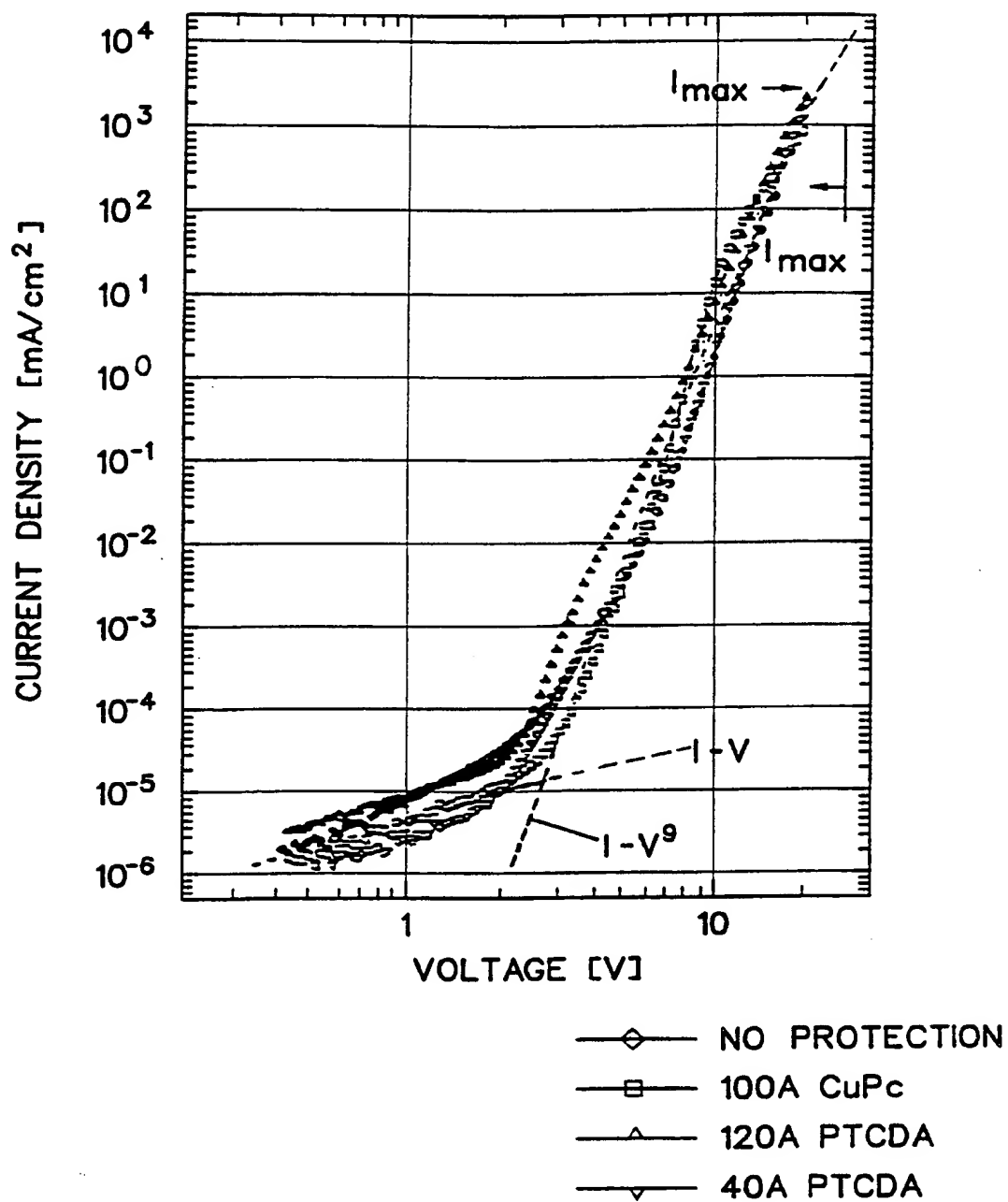
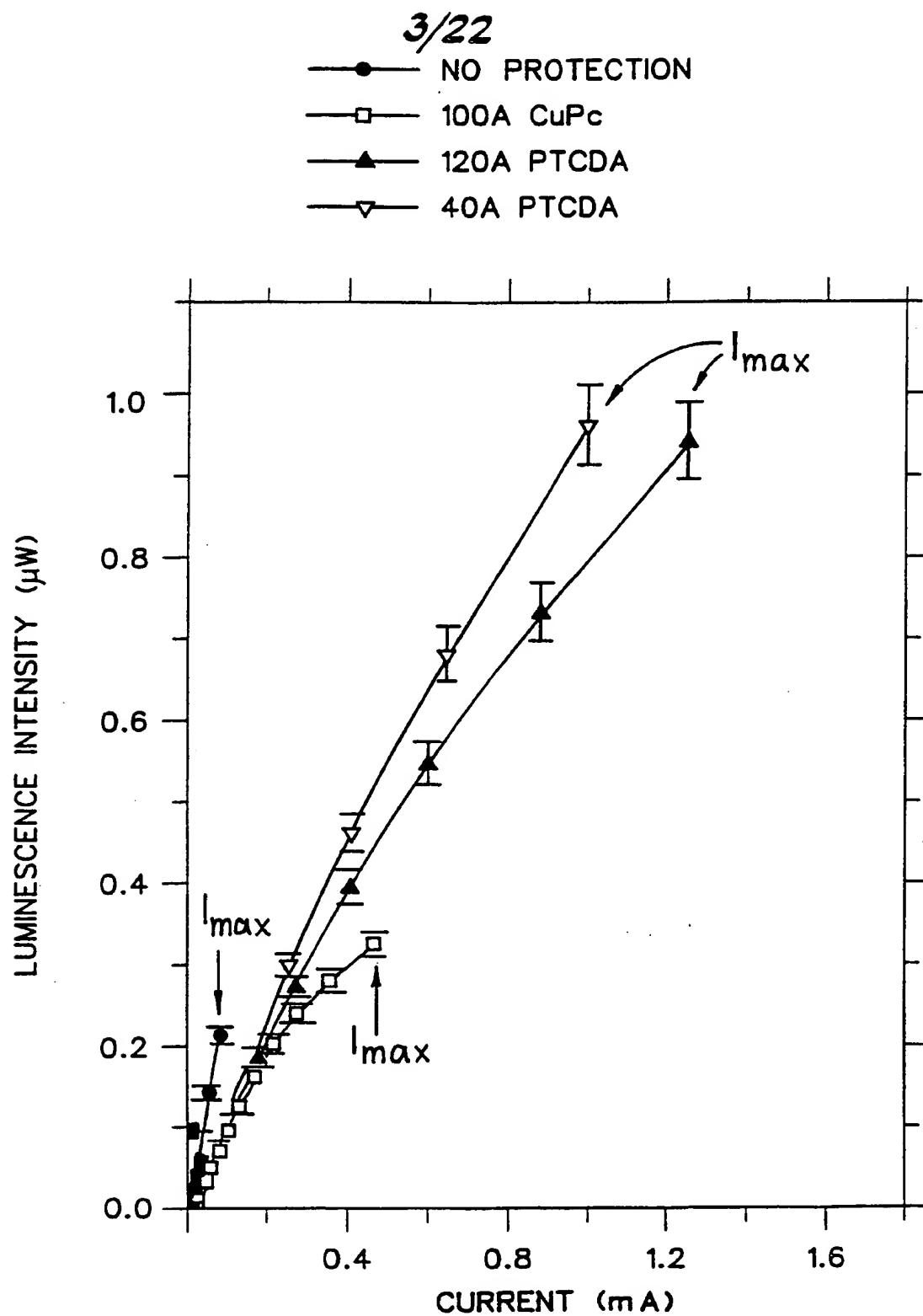


FIG. 2

**FIG. 3**

4/22

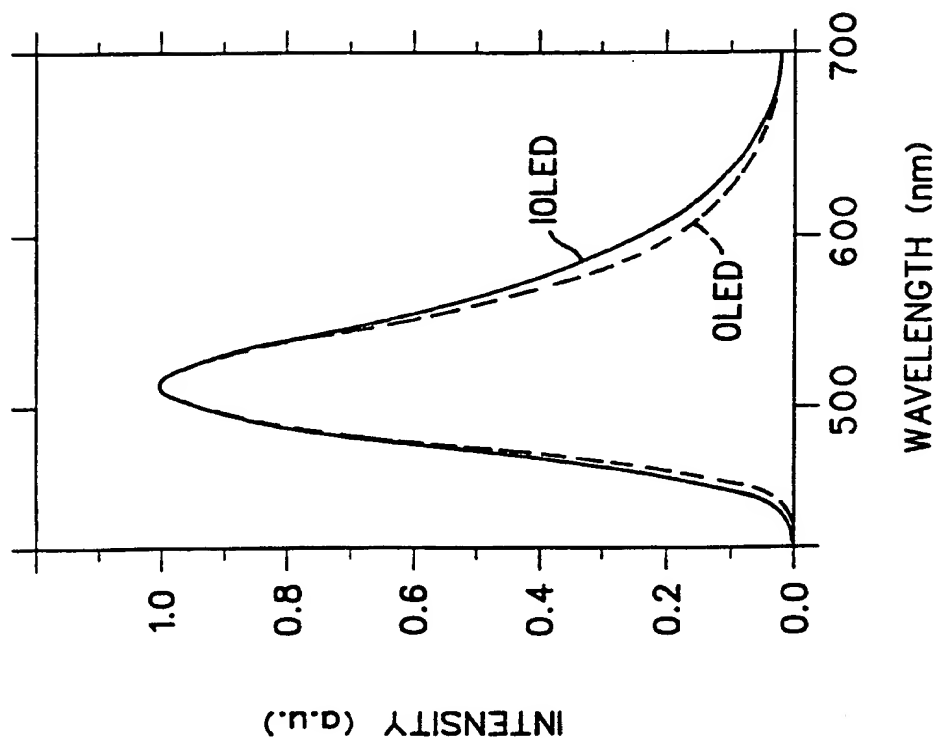


FIG. 4

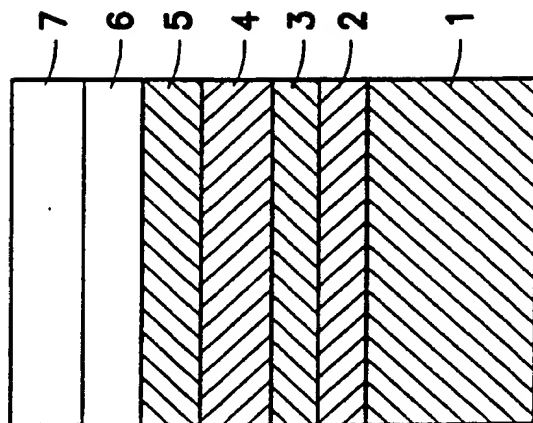


FIG. 6

5/22

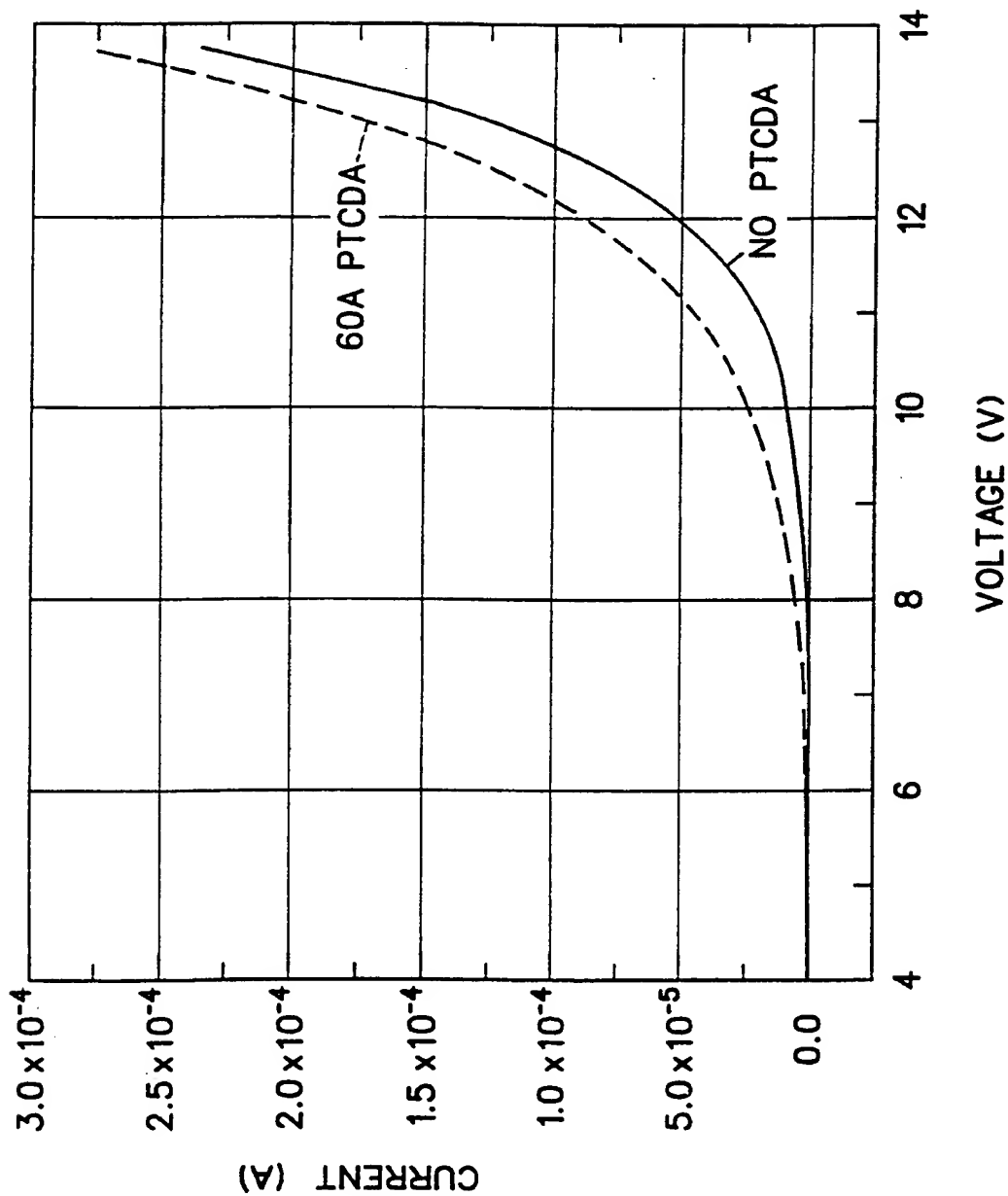


FIG. 5

6/22

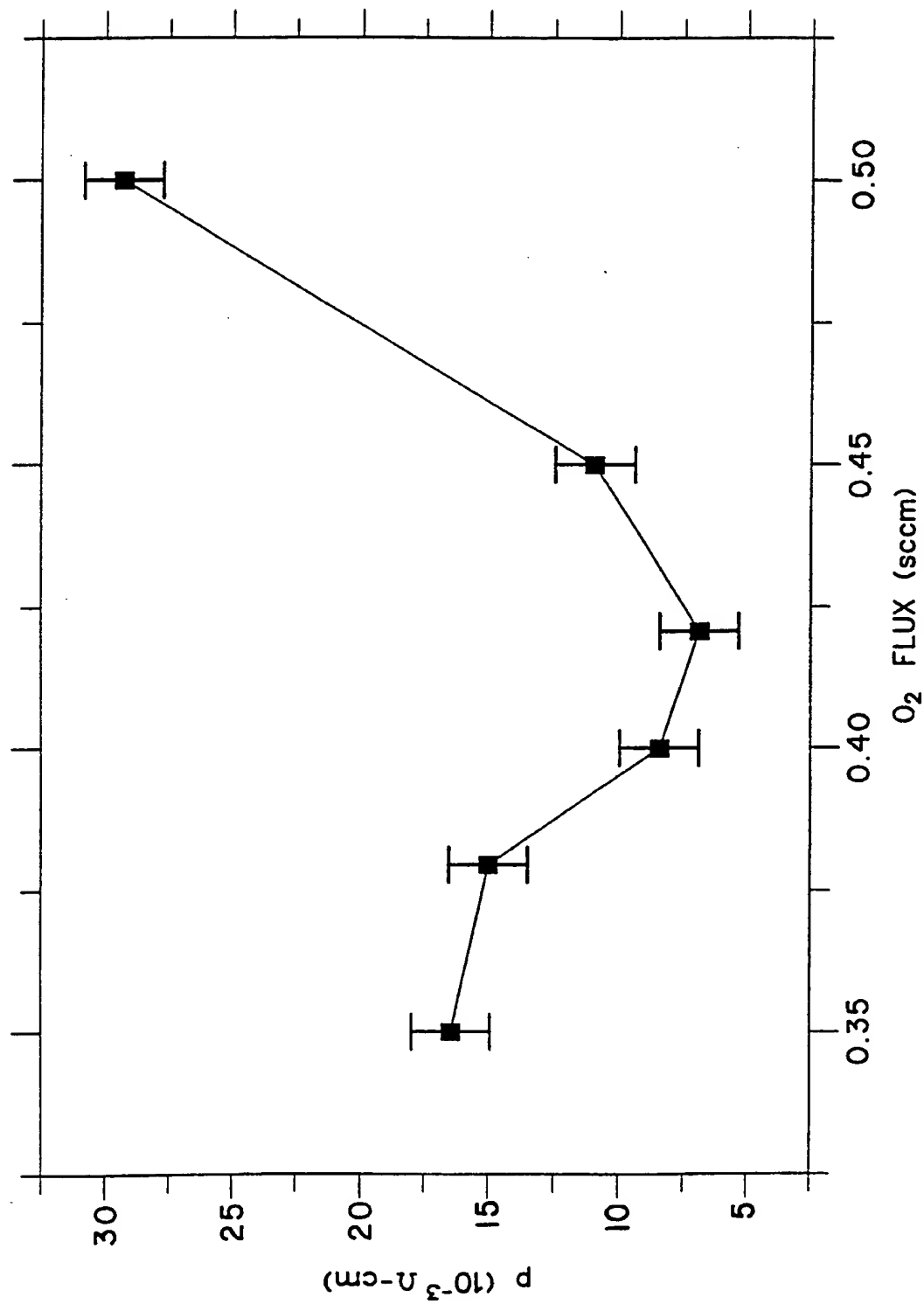


FIG. 7

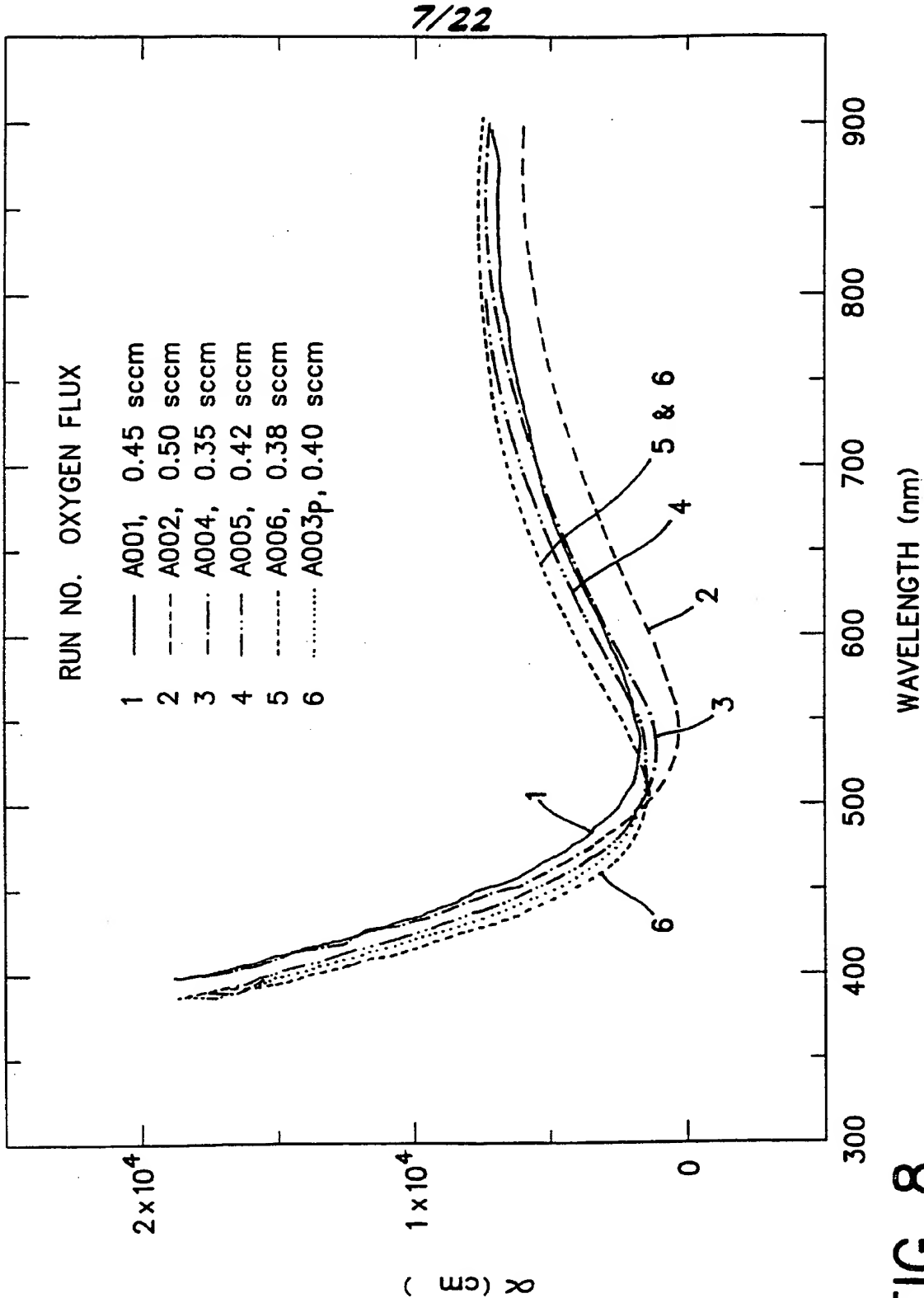


FIG. 8

8/22

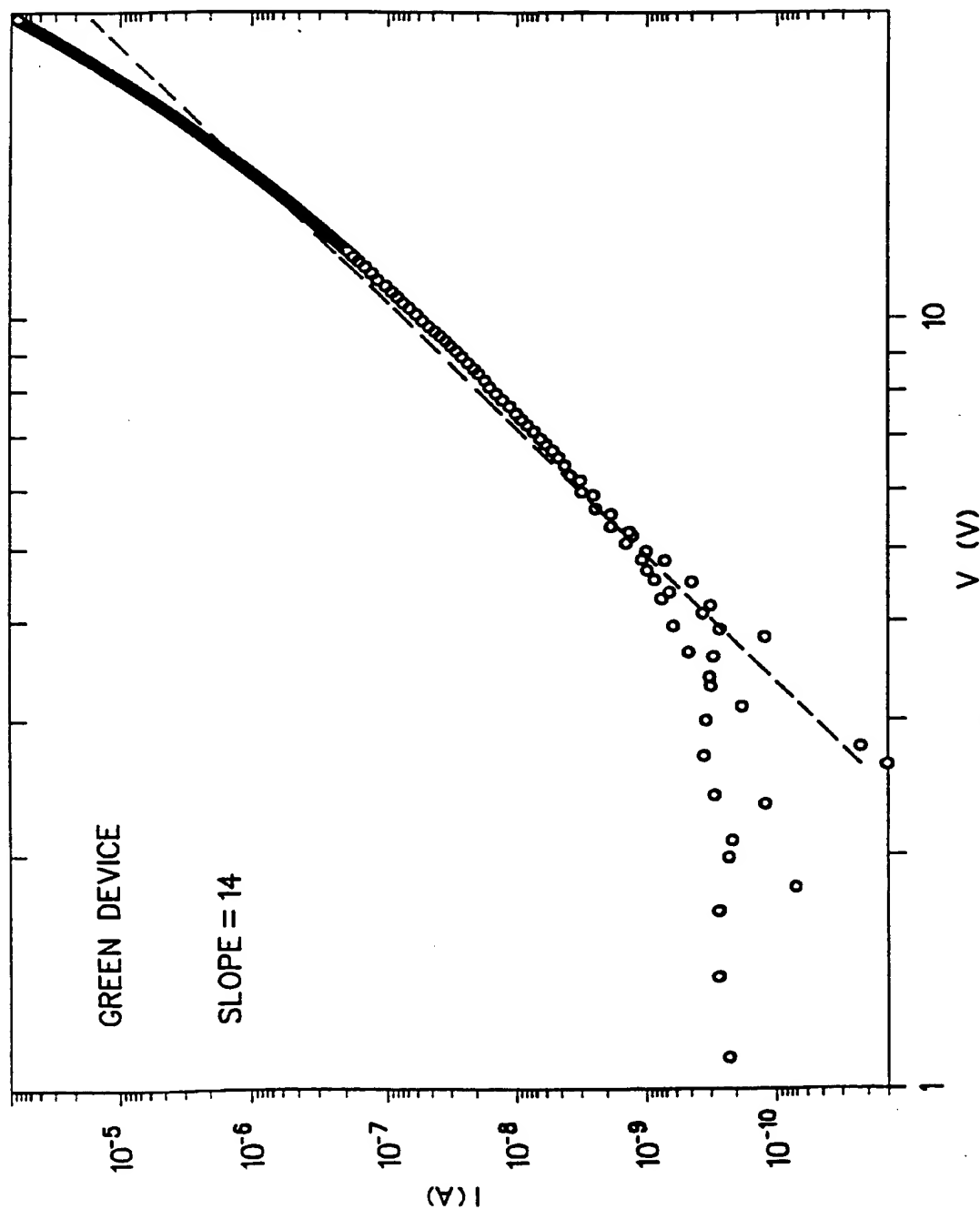


FIG. 9

9/22

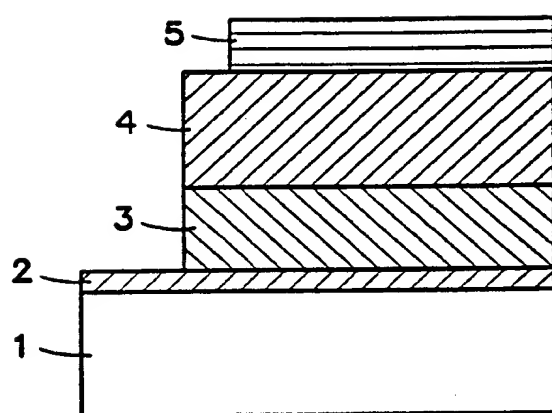


FIG. 10

10/22

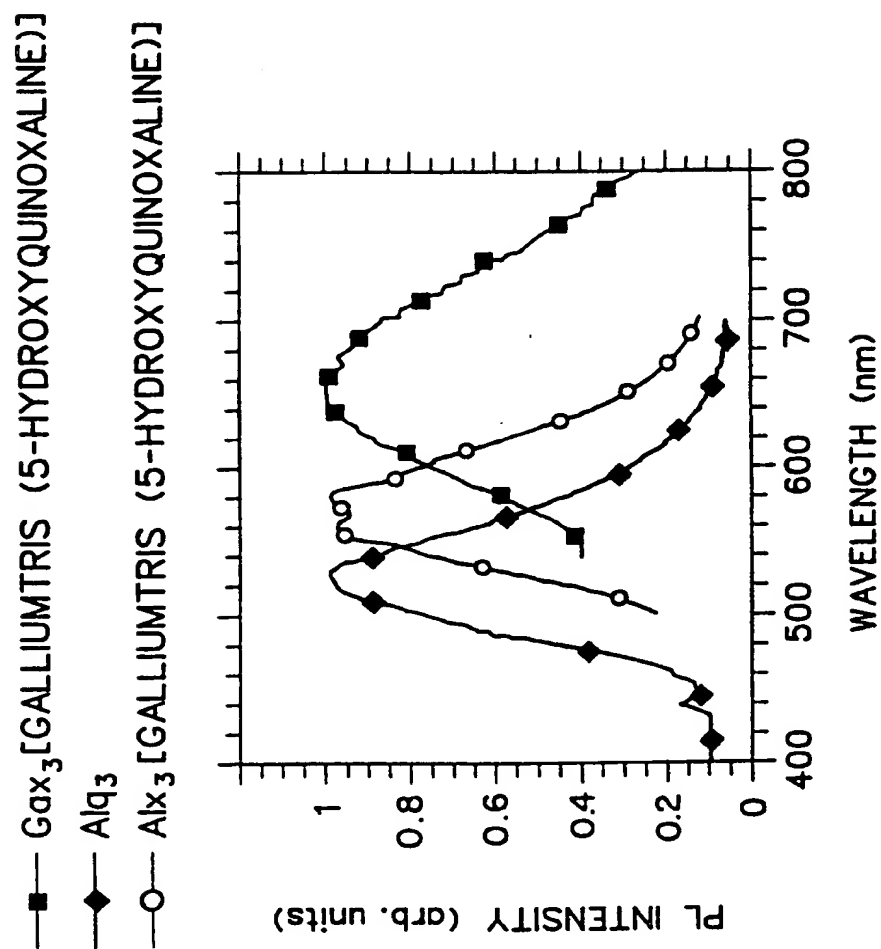


FIG. 11

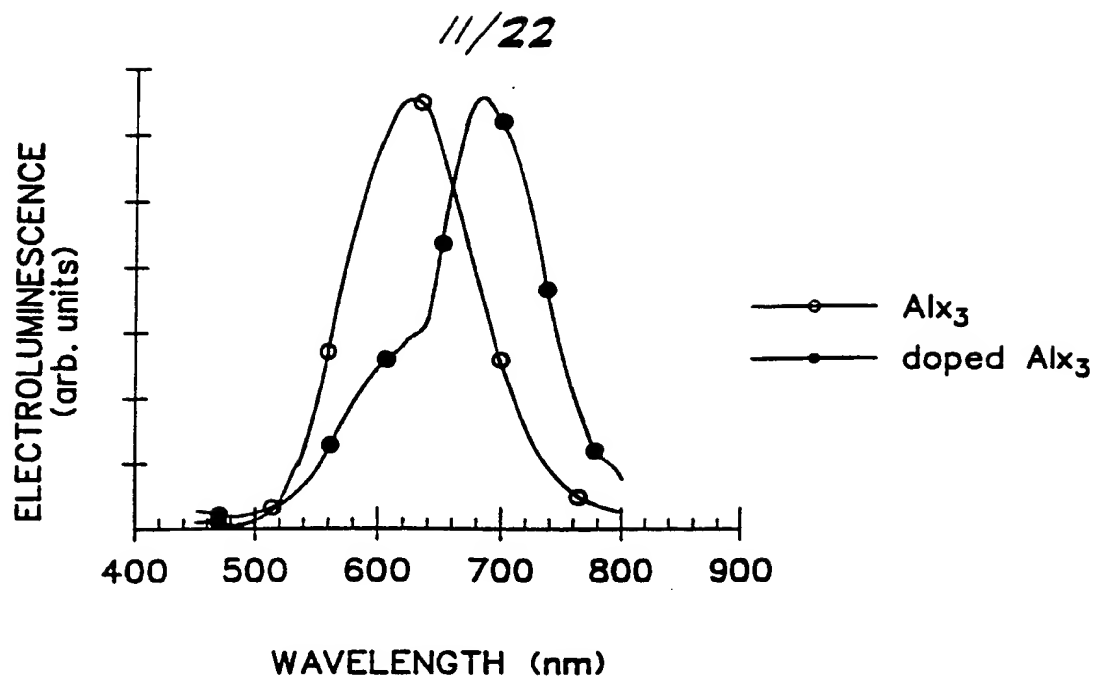


FIG. 12

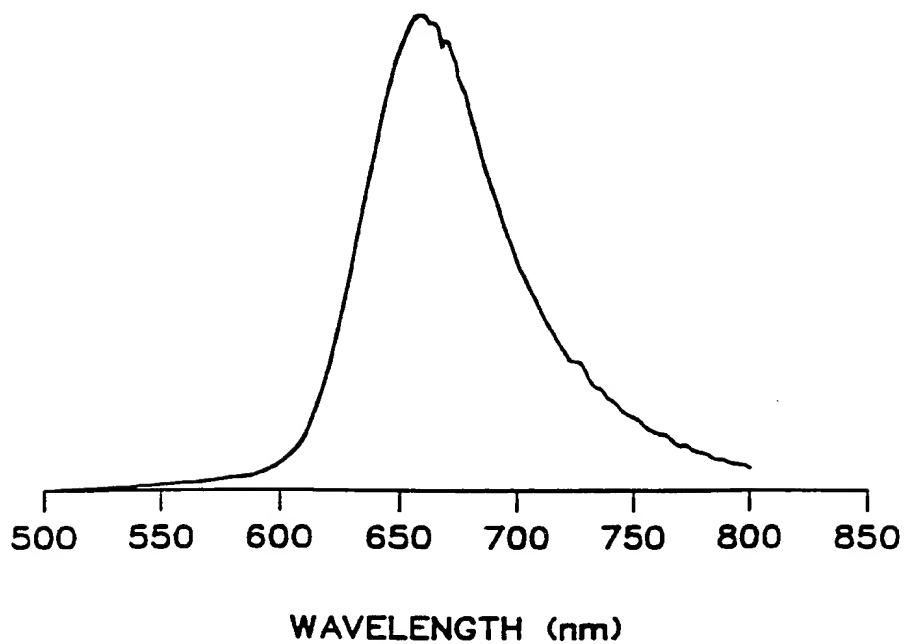


FIG. 19

12/22

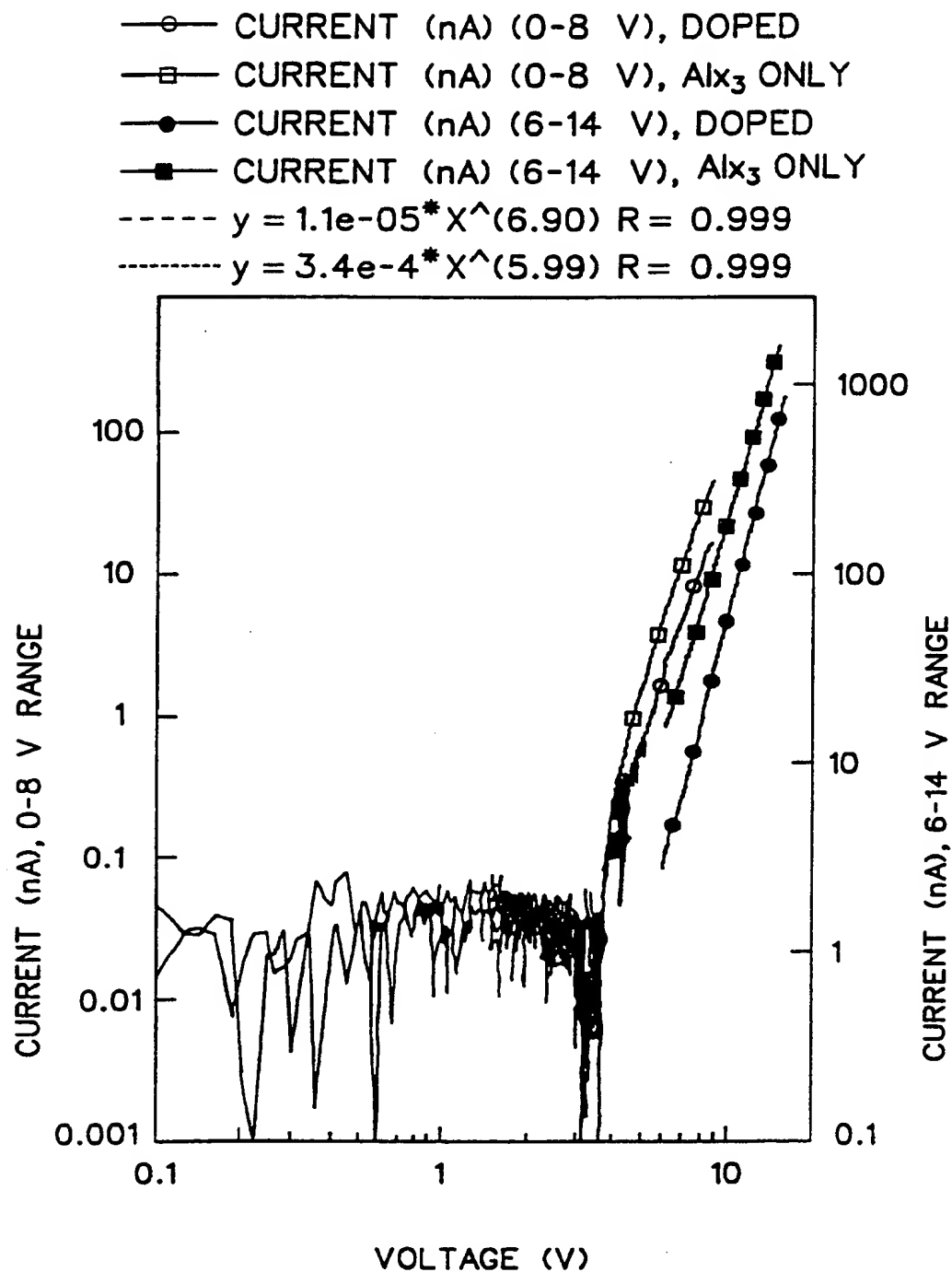


FIG. 13

13/22

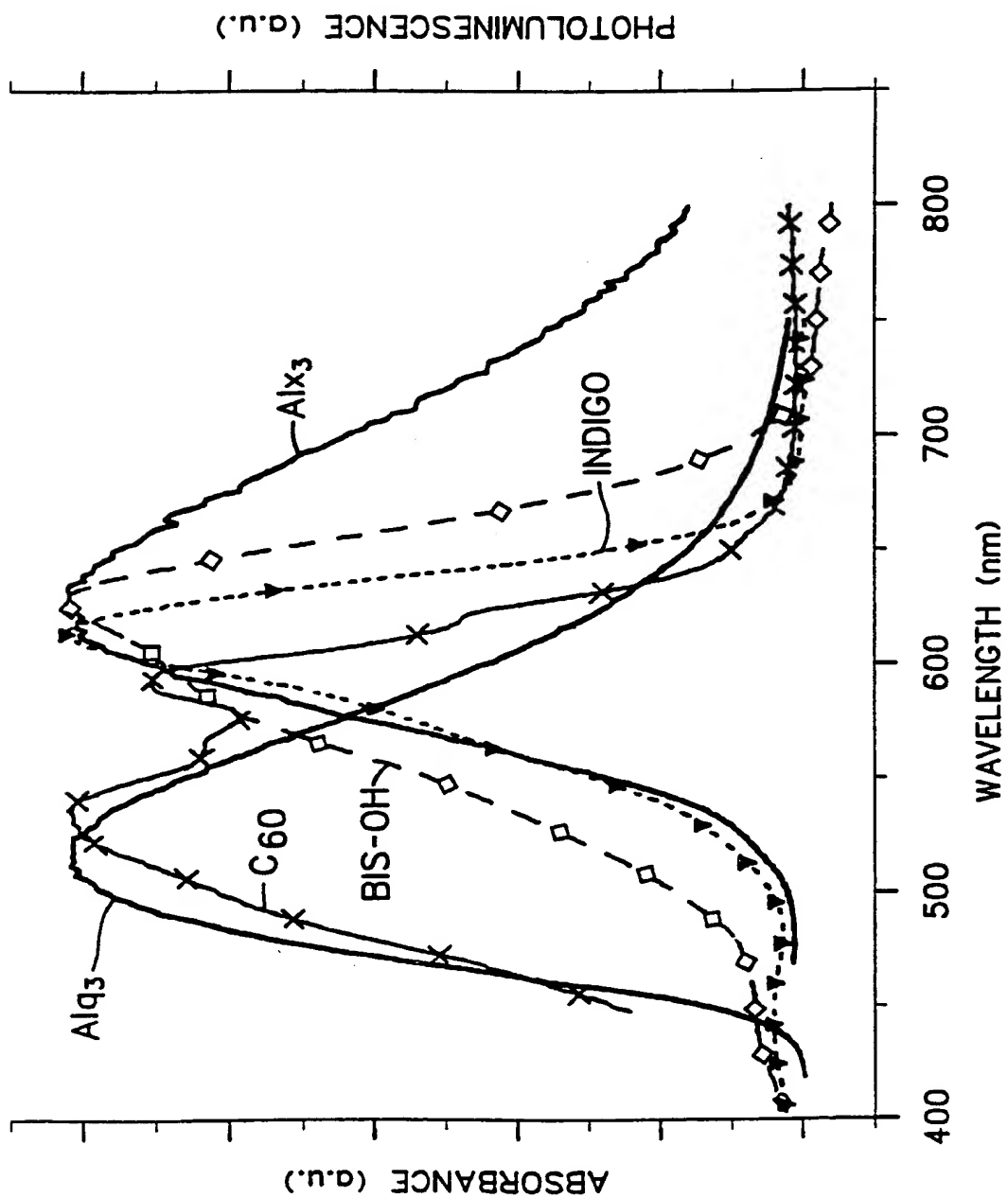


FIG. 14

/4/22

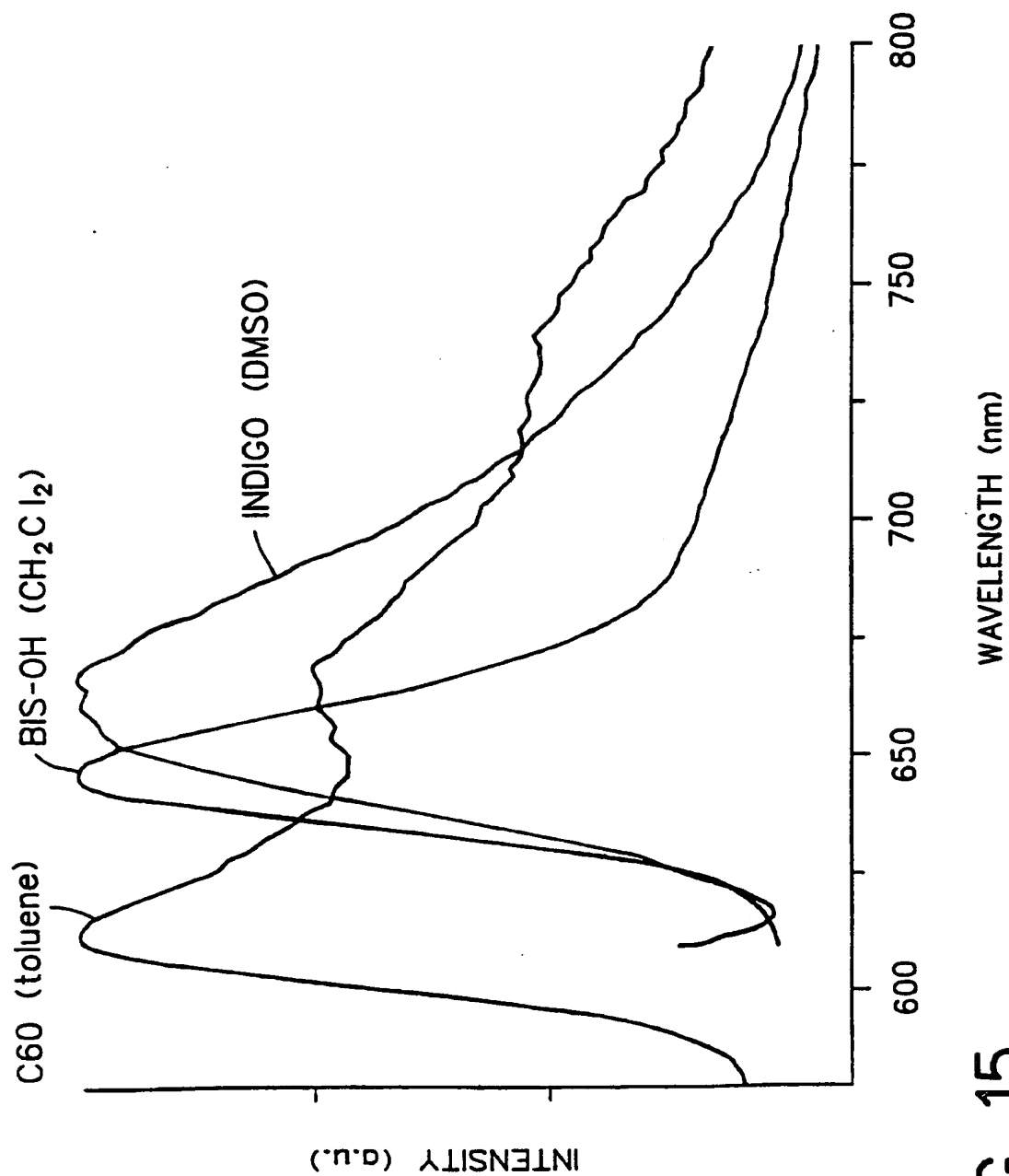


FIG. 15

15/22

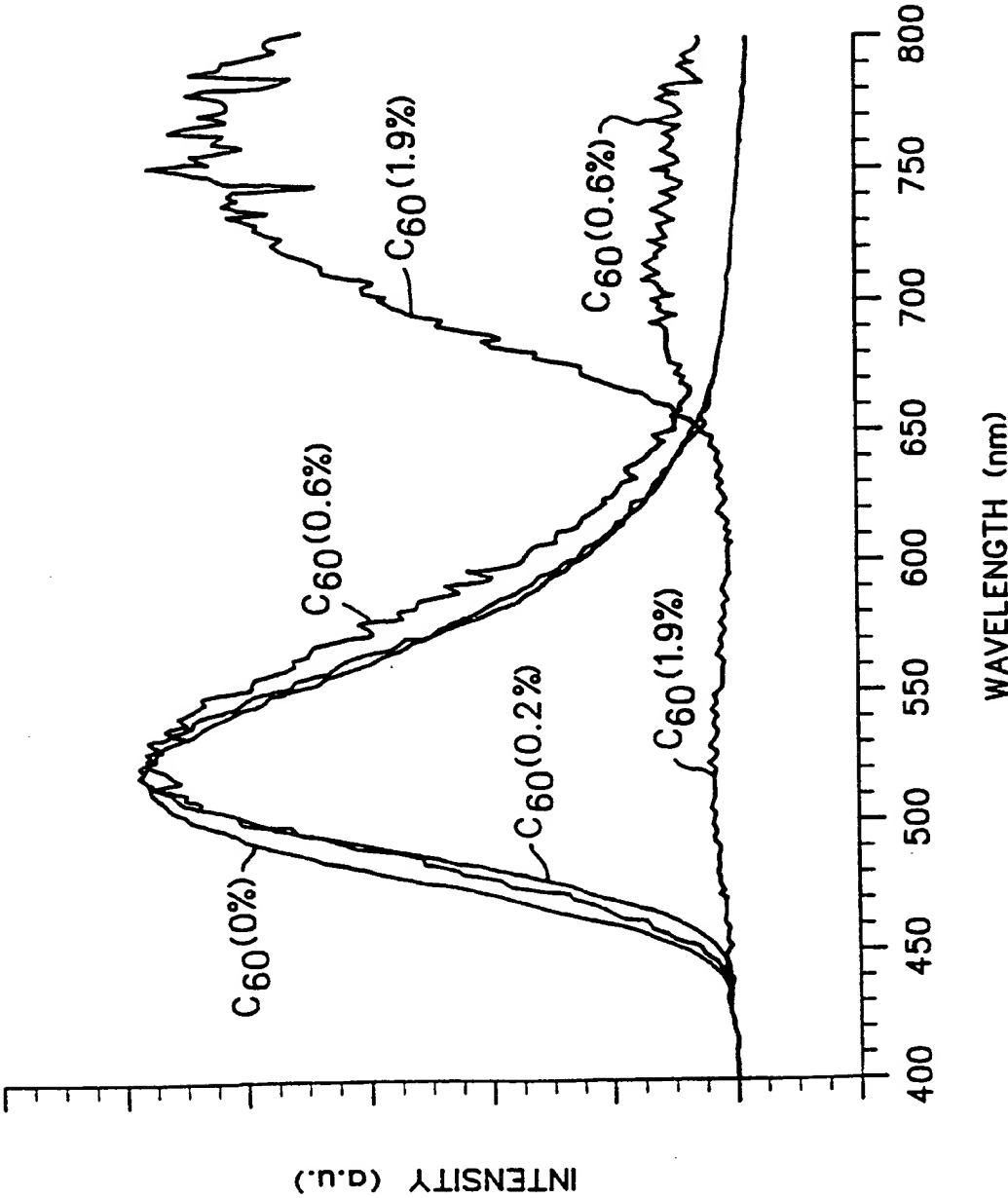


FIG. 16

16/22

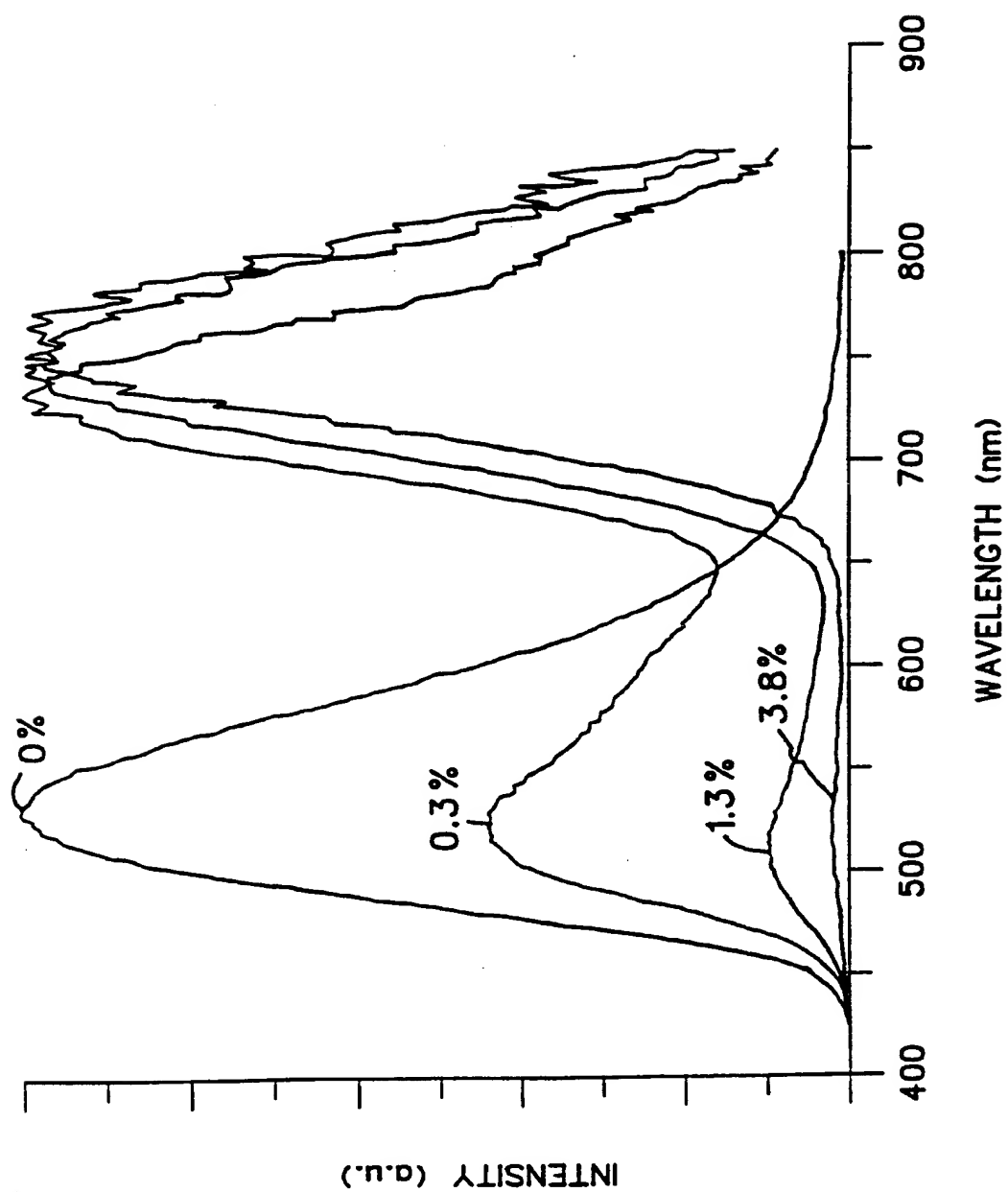


FIG. 17

17/22

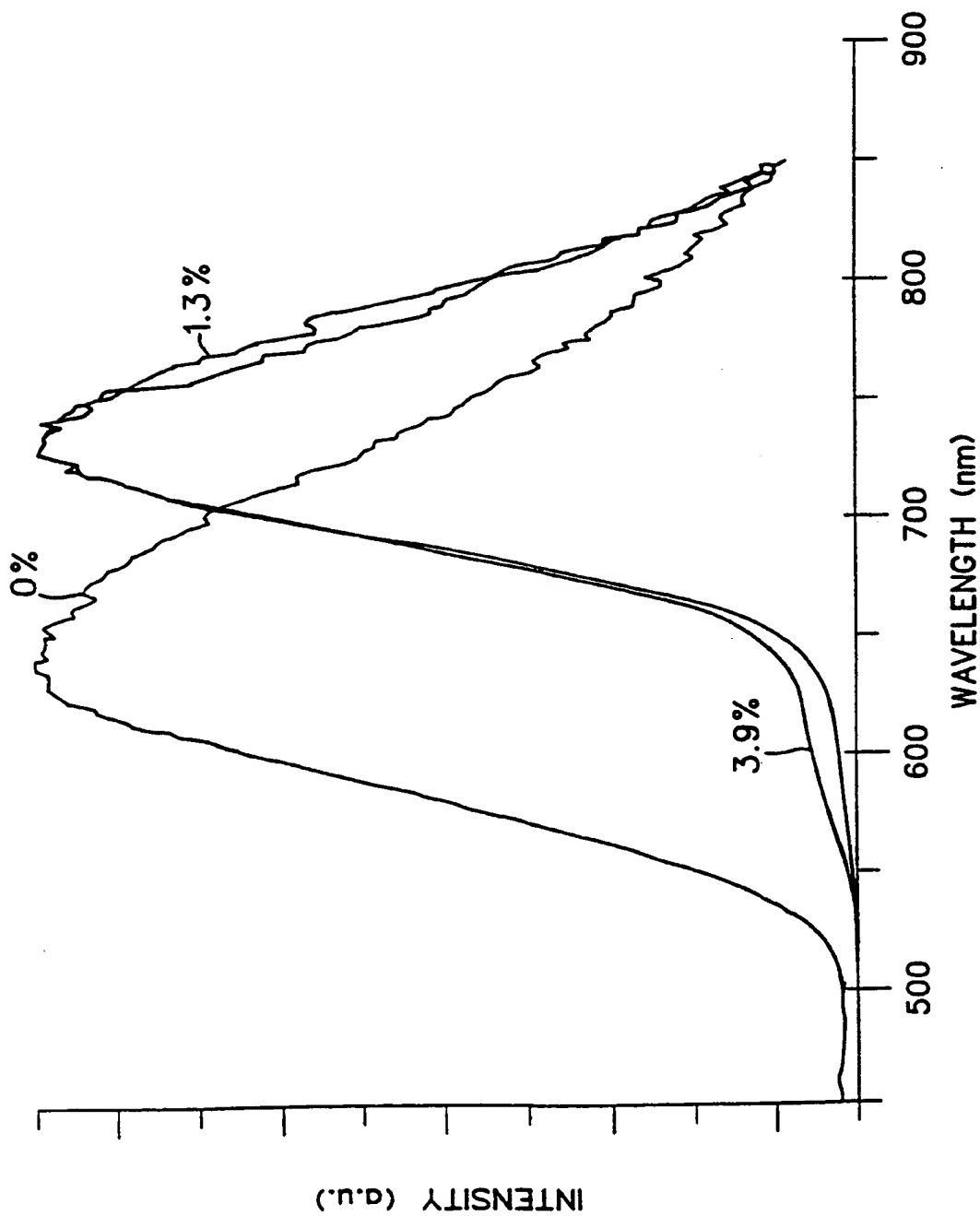
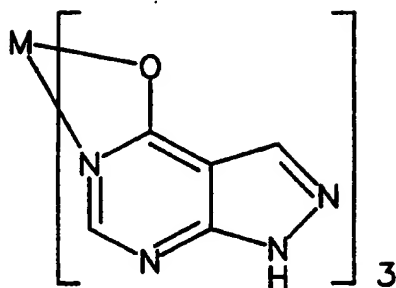


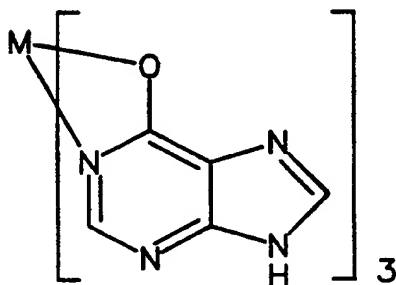
FIG. 18

18/22



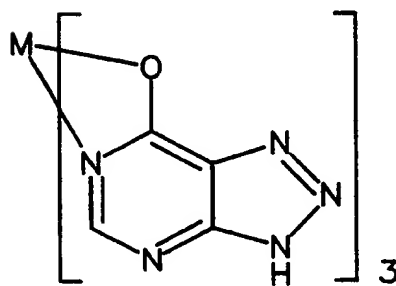
ligand = 4-hydroxypyrazolo(3, 4-d)pyrimidine

FIG.20a



ligand = hypoxanthine

FIG.20b



ligand = azaguanine

FIG.20c

19/22

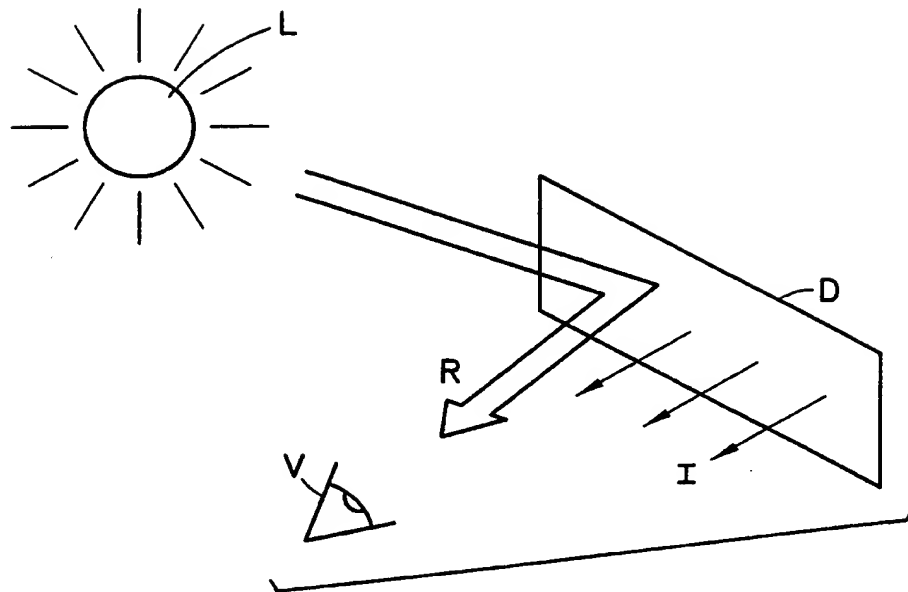


FIG. 21

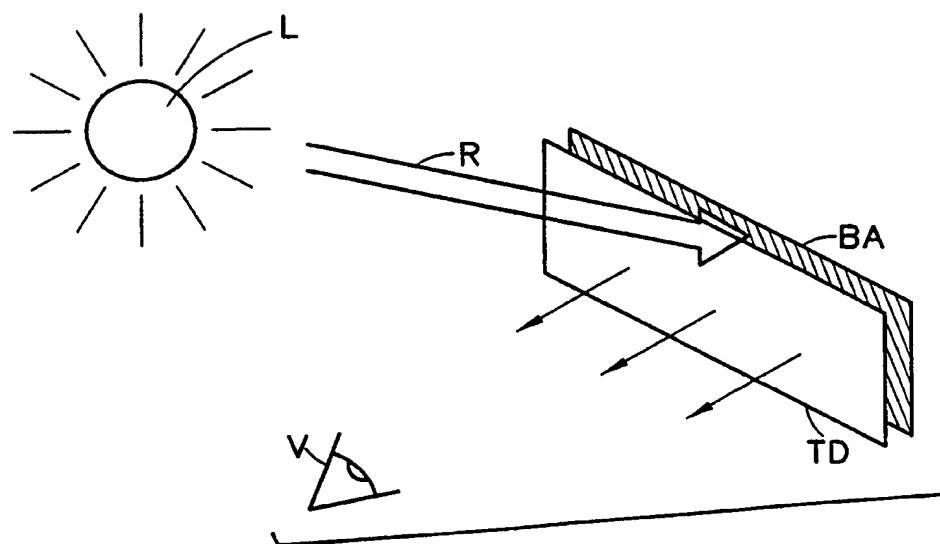


FIG. 22

20/22

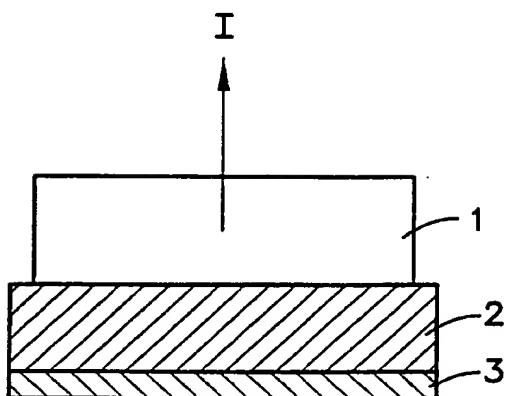


FIG.23

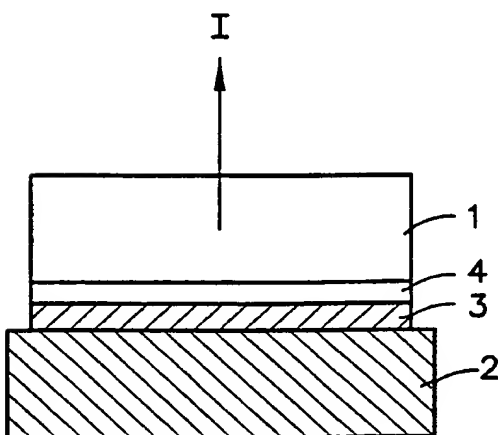


FIG.24

21/22

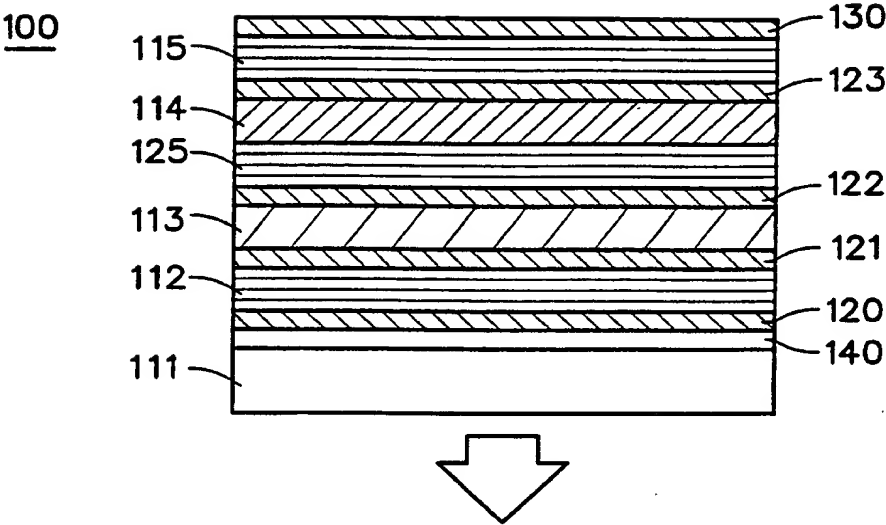


FIG.25

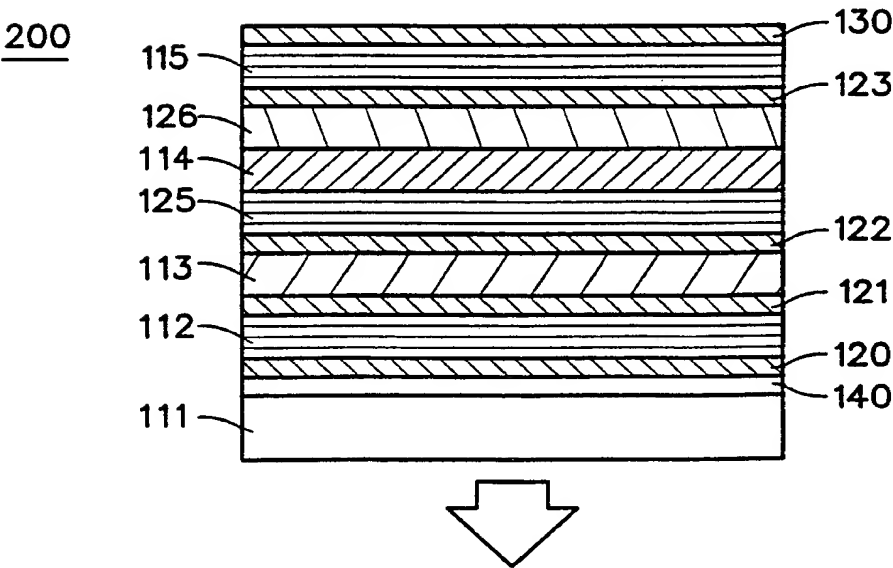


FIG.26

22/22

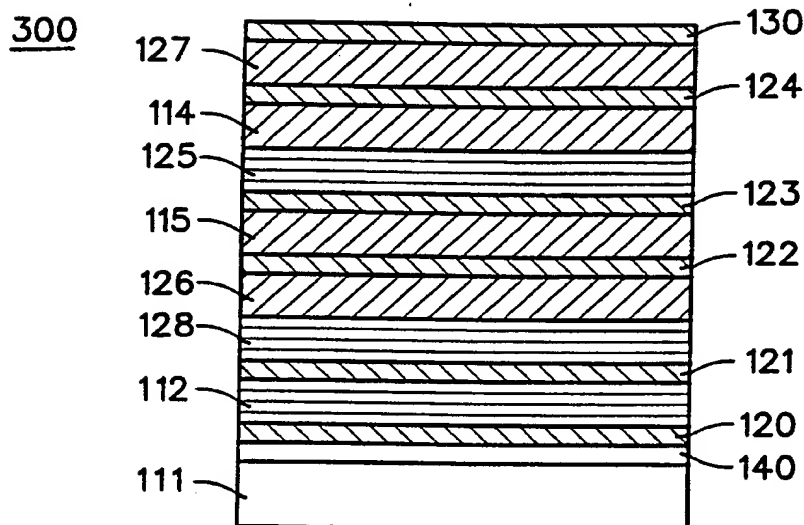


FIG.27

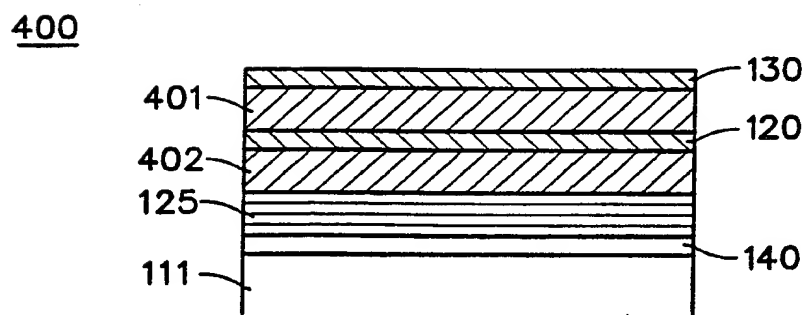


FIG.28

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/23952

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : H01J 1/63; H05B 33/14

US CL : 313/504; 428/690; 450/122; 546/26, 28, 32, 37, 66; 549/232

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 313/504; 428/690; 450/122; 546/26, 28, 32, 37, 66; 549/232

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,950,950 A (PERRY ET AL.) 21 August 1990, whole document.	1-40

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

17 MARCH 1998

Date of mailing of the international search report

27 APR 1998

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

RICHARD L. RAYMOND

Telephone No. (703) 308-1235